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PROTECTION
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Artwork of Rigas Kougkolos

Editor's Preface

"Protection and Restoration of the Environment" is a well-known series of international conferences, organized jointly by one American and one Greek University every two years. It started in 1992, in Thessaloniki, Greece.

The 13th Conference of this series is organized by the Stevens Institute of Technology, USA, the Department of Civil Engineering of the Aristotle University of Thessaloniki, the Department of Civil Engineering of the University of Thessaly and the School of Civil Engineering of the National Technical University of Athens. The conference is designed to facilitate the exchange of ideas and knowledge between diverse groups of the scientific community concerned with current issues in protection and restoration of the environment.

Participation has been very encouraging. Two hundred and sixty papers have been selected for oral or poster presentation, covering a wide range of topics, and reflecting the interdisciplinary nature of environmental challenges. They are classified in the following sessions:

- Water resources management and contamination control (34)
- Wastewater treatment and management (26)
- Protection and restoration of coastal zone and open sea waters (7)
- Protection and restoration of ecosystems (14)
- Solid waste management (15)
- Waste minimization and pollution prevention (11)
- Remediation of contaminated media (7)
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- Global environmental changes (7)
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- Environmental entrepreneurship (7)
- Environmental law and policy (9)
- Cultural and social issues (4)
- Sustainable architecture, planning and development- Spatial and urban planning (14)
- Air quality and contamination control (10)

The conference also hosts four special sessions:

1) Innovative technologies for polluted water remediation, organized by Professor D. Musmarra and by Assistant Professor A. Di Nardo, Second University of Naples, Italy (8)

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2) Environmental aspects of marinas and touristical ports, organized by Professor K. Moutzouris, National Technical University of Athens, Greece (8)
3) Renewable and sustainable energy management and planning, organized by Assistant Professors D. Vagiona and E. Loukogeorgaki, Aristotle University of Thessaloniki, Greece (5)
4) Environmental communication and education, organized by Professor C. Skanavis, University of the Aegean, Greece (10)

The editors would like to thank:

- The authors of the papers, for their scientific contributions
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- The sponsors of the PRE XIII Conference for their financial support, without which it would not have been possible to keep the registration fees at a reasonable level
- All participants for their involvement in the exchange of knowledge, know-how and ideas, which is the essence of this conference
- Grafima Publications for their collaboration as well as their contribution to the editing of both the book of abstracts and the e-proceedings

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Water Resources Management and Contamination Control

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A multi-objective harmony search hybrid for aquifer management

A. Manolis, E. Sidiropoulos*, C. Evangelides

Department of Rural and Surveying Engineering, Faculty of Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
* Corresponding author: Email: nontas@topo.auth.gr

Abstract

A hybrid optimization algorithm has been presented in a previous conference combining harmony search and the Nelder-Mead simplex algorithm. A multi-objective version of this algorithm is presented in this paper. The objective functions considered include pumping and installation costs to be minimized, along with the sum of supply discharges that is to be maximized. Optimal trade-offs among these conflicting objectives are found by determining the corresponding Pareto front. The multi-objective approach presented is compared to standard methods of the literature. The number and position of production wells is addressed as a special feature of the problem.

Keywords: groundwater management; multi-objective optimization; harmony search; evolutionary method

1. INTRODUCTION

Most problems in nature have several objectives to be satisfied. It is obvious that in such a problem, a single solution cannot be found that is better than any other one, especially when these objectives are conflicting with each other. Therefore in a multi-objective problem the term "optimal" cannot be used for a solution and the term "dominant" is used. By definition, a solution dominates another one when the first solution is no worse than the second solution in all objectives and it is better in at least one objective [1]. Thus, for a problem that requires all objective functions to be minimized, a solution x_1 dominates another solution x_2 if:

$$\begin{aligned} \forall i \in \{1, \dots, m\} :\ f_i(x_1) \le f_i(x_2) \wedge \\ \exists j \in \{1, \dots, m\} :\ f_i(x_1) < f_i(x_2) \end{aligned} \tag{1}$$

The solutions that are not dominated by any other solution are known as Pareto – optimal solutions or nondominated solutions [2]. All non-dominated solutions are acceptable, since none of the objective functions can be improved in value without degrading some of the other objective values.

A popular algorithm for solving single-objective optimization problems is Harmony Search Algorithm (HSA) [3]. Recently, a hybrid method was presented that combined the strengths of HSA with those of the Nelder – Mead simplex technique [4]. The method was named Harmony Simplex Hybrid (HSH) and had good results when it was implemented in a test function as well as in a practical single-optimization aquifer management problem [5]. In order to solve the multi-objective optimization problem, the HSH algorithm is transformed based on the ideas used in other algorithms such as Non-Dominated Sorting Algorithm II (NSGA-II) [6], Non-dominated Sorting Hybrid Algorithm (NSHA) [7] and Multi-Objective Harmony Search (MOHS) [8].

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The new algorithm is named Multi-Objective Harmony Simplex Hybrid (MOHSH) and is tested in a similar problem with [5]. In [5], the aquifer management problem is solved by minimizing the cost of well installation and pumping while the total pumping rates of the wells is considered known and steady. In this paper, the total pumping rate is to be maximized while the cost is to be minimized. It is obvious that these objectives are conflicting with each other and therefore the goal is to find a set of nondominated solutions. Well locations, the number of wells and the distribution of pumping rates remain in the problem as optimization parameters.

2. MOHSH ALGORITHM

The Multi-Objective Harmony Simplex Hybrid (MOHSH) algorithm is the result of the application of HSH in multi-objective problems. More information on HSH can be found in [5]. In order to sort the obtained solutions the non-dominated sorting is used as it is described in [6]. The local search by Nelder-Mead algorithm is not applied in every improvisation, giving time to HS to alter the harmonies. The number of improvisations performed by HSA between the local searches is defined in a parameter called NM_st by the user. In addition to the HM, two new slots are kept in memory: the archive [8] and the vault. The size of the archive (AS) is also user defined and the archive is used in order to store the nondominated harmonies. The vault is used to store the solutions of the archive before they are altered by the algorithm, in order to avoid applications of Nelder-Mead to the same harmonies. The steps of the proposed algorithm are as follows:

Step 1: Parameter setting
Define the objective functions, the decision parameters with their boundaries and the parameters of the algorithm.

Step 2. Initialization
Fill the HM matrix with random decision variables in the feasible space. The HM matrix can be described as follows:

$$HM = \begin{bmatrix} x_1^1 & x_2^1 & \cdots & x_n^1 \\ x_1^2 & x_2^2 & \cdots & x_n^2 \\ \vdots & \vdots & \vdots & \vdots \\ x_1^{HMS} & x_2^{HMS} & \cdots & x_n^{HMS} \end{bmatrix} \quad (2)$$

where n is the number of variables and HMS the number of harmonies stored in HM.

Step 3. Archive generation
Evaluate the HMS harmonies and sort them with fast nondominated sorting. The nondominated harmonies move to archive. The empty slots of the HM are filled with randomly generated harmonies until the size of the HM is HMS.

Step 4. Generation of new harmonies
A new harmony is generated HMS times as follows:
for i in range (n):
Select a random harmony from archive x_i^{AR}
Select a random harmony from HM x_i^{HM}
$if\ rand(0,1) < HMCR$:
$x_i^{new} = x_i^{AR} + rand(-1,1) * \left(x_i^{AR} - x_i^{HM}\right)$

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$$if\ rand(0,1) \geq HMCR:$$
$$x_i^{new} = x_i^{min} + rand(0,1) * \left(x_i^{max} - x_i^{min}\right)$$

Step 5. Update of the archive

The new harmonies are evaluated and the combined HM, archive and new harmonies are sorted with fast nondominated sorting.

Step 6. Nelder-Mead implementation

This step is executed every NM_st iterations. The vectors that participate in the local optimization by the Nelder-Mead method are one member from the archive as guide and n members randomly picked from the HM. Whenever a sorting procedure is required from the algorithm, the fast nondominated sorting is applied. In order to avoid the situation where all the vectors of the Nelder-Mead procedure have the same ranking, the harmonies from the archive and HM are added to the sorting. Thus, a more accurate ranking is given to the vectors with little computational cost, since these harmonies are already evaluated.

The procedure is repeated for every harmony in the archive that is not in the vault. The algorithm is terminated if one of the following criteria is met [7]:

i. no solution is dominating another solution.
ii. the simplex size is smaller than a predefined value. This value can be relative to the expected precision.
iii. a user defined number of maximum iterations or function evaluations is reached.

Step 7. Update of the archive and the vault

The harmonies that were optimized locally with the harmonies from HM and the archive are sorted with fast nondominated sorting. The nondominated harmonies fill the archive while the rest fill the HM. If the harmonies in the first nondomination front are more than AS, then the crowded comparison operator [6] is used in order to preserve good distribution of the solutions in the archive. The vault is being replaced by the archive in order to avoid reevaluation of these harmonies from the Nelder-Mead method. If the maximum number of iterations or function evaluations is reached, then the members of the archive compose the calculated nondominated set. If not, the process is repeated from step 4.

3. AQUIFER MANAGEMENT

The basic objectives of groundwater management are usually the minimization of pumping cost and the maximization of total pumping rate. In order to estimate the optimal trade-offs between these conflicting targets the MOHSH and the MOHS algorithms are used.

3.1. Problem definition

A semi-infinite unconfined aquifer is considered that was studied in [5]. In that study the objective was to minimize the pumping and installation cost of the wells while the total pumping rate was known. In this paper the total cost is to be minimized also, while the total pumping rate is to be maximized. Details about the problem can be found in [5].

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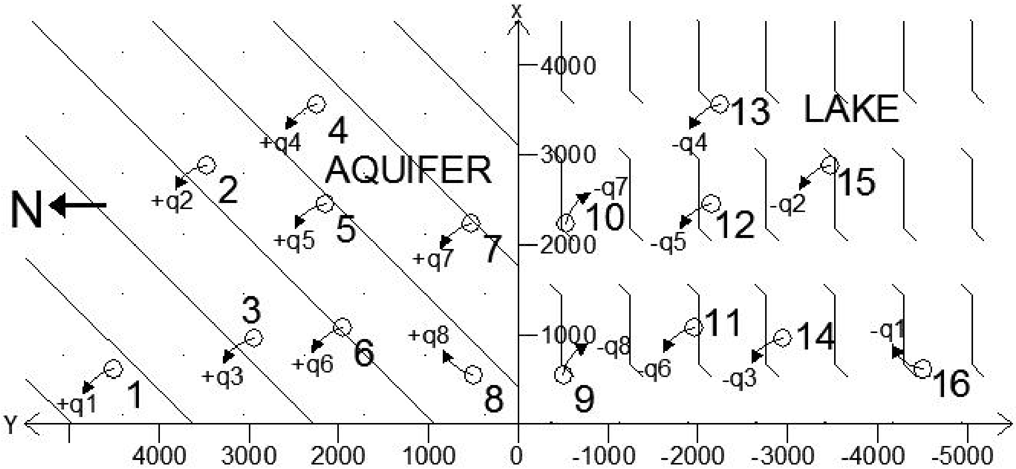


Figure 2. Plan view of the aquifer and locations of candidate wells

The locations that are shown in Figure 1 are candidate locations of the wells. The number of the wells, their final location and the pumping rate distribution are to be determined during the optimization process. The parameters used by the algorithms are as shown in Table 1.

Table 1. Parameters setting

PARAMETER	ABBREVIATION	VALUE
Harmony Memory Size	HMS	50
Archive Size	AS	100
Maximum Improvisations	MI	1000
Harmony Memory Consideration Rate	HMCR	0.9
Maximum Iterations of Nelder-Mead	MINM	20
Number of iterations between Nelder - Mead	NM_ST	10
Precision of variables	PREC	1 m^3/day

4. RESULTS – DISCUSSION

In order to evaluate the results the C metric function is used. It is defined as follows [8]: Let $X', X'' \subseteq X$ be two sets of decision vectors. The function C maps the ordered pair (X', X'') to the interval [0,1].

$$C(X', X'') = \frac{|a'' \in X''; \exists a' \in X': a' \prec a''|}{|X''|} \tag{3}$$

The value $C(X', X'') = 1$ means that all solutions of X'' are dominated by solutions from X'. The opposite condition $C(X', X'') = 0$, means that there is no solution in X'' dominated by any solution in X'. Notably, both $C(X', X'')$ and $C(X'', X')$ have to be calculated since $C(X', X'')$ is not necessarily equal to 1- $C(X'', X')$.
Each algorithm runs 30 times. For each run, there is a C value for each ordered pair. The results are shown in Table 2.

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Table 2. Results of C function calculation

RUN	C(MOHSH,MOHS)	C(MOHS,MOHSH)		RUN	C(MOHSH,MOHS)	C(MOHS,MOHSH)
1	0.74	0		16	0.66	0
2	0.72	0		17	0.88	0
3	0.84	0		18	0.82	0
4	0.66	0		19	0.8	0.02
5	0.86	0		20	0.72	0
6	0.84	0		21	0.84	0
7	0.82	0		22	0.78	0
8	0.86	0		23	0.68	0
9	0.9	0		24	0.7	0
10	0.62	0		25	0.48	0
11	0.64	0		26	0.92	0
12	0.72	0		27	0.74	0
13	0.76	0		28	0.74	0
14	0.76	0		29	0.62	0
15	0.76	0		30	0.84	0

It can be seen clearly that the solutions obtained from the proposed algorithm MOHSH tend to dominate over the solutions from MOHS in the problem presented here. On the contrary, there is only one solution of the MOHSH on the 19th run that is dominated by a solution of MOHS. On the other hand, MOHSH has a higher complexity than MOHS due to the addition of the Nelder-Mead method. The present results are promising and more numerical experimentation would be useful, in order to establish the performance of the proposed method.

References

[1] Zitzler E., Deb K., Lothar T., 2000. Comparison of multiobjective evolutionary algorithms: Empirical results. *Evolutionary Computation*, **8(2)**, 173 – 195.

[2] Lee K.S., Geem Z.W., 2004. A new meta-heuristic algorithm for continues engineering optimization: harmony search theory and practice. *Comput. Meth. Appl. Mech. Eng.* **194**, 3902-3933.

[3] Chankong & Haimes, 1983. *Multiobjective decision making theory and methodology*. New York: North-Holland.

[4] Nelder J. A., Mead R., 1965. A simplex method for function minimization. *Comput. J.* **7**, 308-313.

[5] Manolis A., Sidiropoulos E., 2015. A harmony search hybrid for aquifer management. *Proceedings of the International Conference on Protection and Restoration of the Environment XII.*

[6] *Deb K., Pratap A., Agarwal S., Meyarivan T., 2002. A fast and elitist multiobjective genetic algorithm: NSGA-II. IEEE Transactions on evolutionary computing, 6(2), 182-197.*

[7] *Ghiasi H., Pasini D., Lessard L., 2012. A non-dominated sorting hybrid algorithm for multi-objective optimization of engineering problems. Engineering optimization, 43(1), 39-59.*

[8] Sheng W., Liu K., Li Y., Liu Y., Meng X., 2014. Improved multiobjective harmony search algorithm with application to placement and sizing of distributed generation, *Mathematical problems in engineering*, Article ID 871540.

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Management strategy for fragile aquatic ecosystems and water resources: A "tool" for the reduction of manmade eco-environmental impact on the lakes, lagoons and marshes in Attica region

A. Mertzanis[1*], F. Marabini[2], M. G. Angeli[3], A. Mertzani[4], F. Pontoni[5], P. Gasparetto[6]

[1] Technological Educational Institute of Central Greece, Department of Forestry and Management of Natural Environment, GR-36100, Karpenisi, Greece
[2] National Research Council, Institute for Marine Science (ISMAR-CNR), 101 P. Gobetti str., 40129, Bologna (BO), Italy
[3] National Research Council, Research Institute for Hydrogeological Protection (IRPI-CNR), 06128, Via Madonna Alta, 126 Perugia (PG), Italy
[4] National Technical University (NTUA), School of Electrical and Computer Engineering, Zografou Campus, Heroon Polytechniou 9, GR-15780, Zografou, Greece
[5] Geoequipe S.T.A., Sandro Pertini str., Tolentino (MC), Italy
[6] IQT Consulting S.r.l., Rovigo (RO), Italy
*Corresponding author: Email: arismertzanis@gmail.com

Abstract

The designation and assessment of the causes deteriorating the fragile aquatic ecosystems and water resources are among the first stages of strategic management. They constitute an important tool for the strategic management of the environment and the above mentioned aquatic ecosystems and water resources.

The appropriate management of these ecosystems and water resources can facilitate the mitigation and reversal of the eco-environmental impact caused by anthropogenic interventions in the drainage basins. These strategic management "tools" for aquatic ecosystems and water resources also employ advanced hydrological models in combination with the recording and systematic monitoring of qualitative and quantitative environmental parameters (level of pollution, eutrophication, water level, water volume, temperature, stratification of water column, pH, salinity, water renewal rate, geomorphological changes, sediment transport rate, coastal erosion rate etc.).

The region of Attica hosts a number of fragile aquatic ecosystems and water resources, including natural lakes, lagoons, marshes and some dams (water supply dams, flood barriers, water storage basins, etc.). Smaller wetlands can also be found in various locations especially in the coastal zone. Typical examples of these fragile aquatic ecosystems would be the protected wetland (Mega Elos) located in the National Park of Schinias-Marathon and the lakes Koumoundourou and Vouliagmeni, both consisted of a mixture of salt and fresh water. An important water resource for the Attica region is the Lake Marathon (Limni Marathonos), a water supply reservoir, formed by the construction of Marathon dam, in the Oinois river valley (r. Haradros) in East Attica.

The main purposes of the present research are to: a. highlight the manmade interventions, b. evaluate the impact on the fragile ecosystems and water resources and c. describe a strategy for the mitigation of the manmade eco-environmental impact, in order to propose improvements over the sustainable management of the fragile aquatic ecosystems in the Attica region.

Keywords: Attica region; lagoons; lakes; manmade interventions; marshes

1. INTRODUCTION

It has been observed that anthropogenic pressures and interventions in recent decades, such as intensification and development of agriculture projects, embankments, exsiccation, wood cutting, deforestation, industrial sittings, urban and touristic development, dams and reservoirs, uncontrolled watering from surface water tables and uncontrolled pumping of underground waters, may seriously affect the environmental balance of inland and coastal environments (wetlands, lagoons, Deltas, estuaries and coastal areas)[1]. These uncontrolled anthropogenic pressures and interventions in several cases cause fragile aquatic ecosystems and water resources degradation and loss by changing water quality, quantity, and flow rates; increasing pollutant inputs; and changing species composition as a result of disturbance and the introduction of nonnative species [2]. Also, these anthropogenic activities may lead to environmental degradation of river waters, lakes and lagoons or hydro-geomorphological changes and constitute the cause of environmental destabilization [3].
The region of Attica hosts a number of fragile aquatic ecosystems and water resources, including wetlands, lagoons, marshes and some dams (water supply, flood control dams, water storage basins, etc.). Smaller wetlands can also be found in various locations especially in the coastal zone. Typical examples of these fragile aquatic ecosystems would be the protected wetland (Mega Elos) located in the National Park of Schinias-Marathon and the lakes Koumoundourou and Vouliagmeni, both consisted of a mixture of salt and fresh water. An important water resource for the Attica region is the Marathon Lake, a water supply reservoir, formed by the construction of Marathon dam, in the Inois river valley in northeastern Attica.

The timely and accurate information regarding multiple stressors causing deterioration on fragile aquatic ecosystems and water resources, the proper environmental impact assessment and the systematic monitoring can provide important input to managing and mitigating the negative effects of human land management and freshwater ecosystems and sensitive wetland habitats.

2. MATERIALS AND METHODS

2.1 Research site location

This paper deals with the fragile aquatic ecosystems and water resources, i.e. the wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes, in Attica region. Most of these ecosystems, have suffered serious alterations from the manmade interference, in the wider area or on their coastal zone. This study mainly focuses in some wetlands which have undergone alterations due to anthropogenic pressures and interventions. These fragile aquatic ecosystems (wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes), should be located in Attica region and especially: 1. Asopos river delta-estuaries (1AttiWETL) near Halkoutsi at South Euboean gulf, 2. Oropos lagoon (2AttiWETL), near Ag. Konstantinos and northeastern of Halkoutsi at South Euboean gulf, 3. Schinias marsh (Mega Elos)(3AttiWETL) located in the National Park of Schinias-Marathon at Marathon gulf (South Euboean gulf), 4. Mega Rema marsh (4AttiWETL) Mega rema of Rafina stream estuaries in Rafina at South Euboean gulf, 5. Artemida marsh (Loutsa)(5AttiWETL) in Artemida at South Euboean gulf, 6. Vravrona marsh (6AttiWETL) near Vravrona and Poria at South Euboean gulf, 7. Alykes of Anavyssos marsh (7AttiWETL) in Anavyssos at Saronikos gulf, 8. Anavyssos lagoon (8AttiWETL) southwestern of Anavyssos at Saronikos gulf, 9. Lagonisi lagoon (9AttiWETL) in Lagonisi at Saronikos gulf, 10. Vouliagmeni lake (10AttiWETL) southeastern of Vouliagmeni at Saronikos gulf, 11. Koumoundourou lake (11AttiWETL) near Skaramangas and Aspropyrgos at Elefsina gulf, 12. Vourkari marsh (12AttiWETL) near Megara and Nea Peramos at Elefsina gulf, 13. Psathas marsh (13AttiWETL) near Alepochori and Porto Germeno at Korinthiakos gulf, 14. Psiphta lagoon (14AttiWETL) northwestern of Troizina at Epidavros gulf, 15. Troizina marsh (15AttiWETL) northeastern of Troizina at Saronikos gulf, 16.

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Alyki lagoon (16AttiWETL) southeastern of Galatas at Aegean sea [4,5]. In the Attica region have been constructed and operate, as mentioned below dams and reservoirs (artificial lakes), which are used for various uses (water supply, flood control dams, water storage basins, etc.): 1. On the main river channel of Inois has built and operates the water supply dam “Marathon” (1AttiArtL). The construction of this dam was completed in 1929. 2. In the Rapentosa Basin, near Vranas, in 2004, has built and operates the “Rapentosa” flood control dam (2AttiArtL). 3. At the northeastern side of Mount Parnitha, in Ippokrateios Politeia, has formatted, in 1975, an artificial lake (Beletsi lake)(3AttiArtL) the waters of which are used for the fire protection of Mt. Parnitha. The Schinias Olympic Rowing and Canoeing Centre was built to host the rowing and canoe sprint events at the Summer Olympics (2004) in Greece. It covers 1.24 km² [6,7,8,9].

It should be noted that Inois river is one of the biggest rivers of Attica. Inois estuary includes the mouth of Inois river or Haradros to the Marathon bay in the northeastern coastal area of Attica, the Marathon coastal plain, the desiccated Vrexizas fen (before the decade of 1960) to the southwest of the Inois river mouth, the Schinias marsh, as well as the pine forest (*Pinus pinea & Pinus halepensis*). It drains an area of almost 177.2 km^2 in northeastern Attica and discharges at Marathon gulf. The terrestrial part of the coastal zone of the Marathon gulf of is of low relief, consisting of low-lying terraces, alluvial plains, valleys and eroded plain-surfaces. The subaerial part of the zone is sandy having its larger width at its northern part; some 25 m. The backshore is associated with a low-relief sand dune field which is better developed to the north Haradros mouth area, where the well-known pine-tree forest occupies the dune field [10]. The northeastern part of the area includes the Schinias-Marathon National Park, which is a protected area (Natura 2000: GR 3000003). This protected area is one of the most important ecosystems in Greece (Figures. 1,2,3,4&5).



Figures 1,2,3&4: Schinias marsh (Mega Elos) and pine forest (*Pinus pinea & Pinus halepensis*) in the National Park of Schinias-Marathon (3AttiWETL) at Marathon gulf (Figures 1,2&3, Photos by Asimina Mertzani)(Figure 4, Source of aerial photos: TripInView/Geotag Aeroview 2014).

National Park of Schinias-Marathon (Natura 2000: GR 3000003): A wetland with sweet, salty and brackish water, reeds, trees, halophytic vegetation and wet meadows, which floods regularly. The wetland of Schinias is consisting of a marine bay into a lagoon and a marsh with bilateral

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supply from the shore (torrents and springs) and the sea. The wetland of these ecosystem hosts a large number of migratory birds during the migration seasons and attracts thousands of visitors and birdwatchers every year and is equipped with special observatory view posts. The wetland performs a number of valuable ecological functions: Supports wide variety of life, holds rainwater, enriches with this aquifer and ensures the balance of the climate. After the hydraulic works, that were implemented, (broaching of drainage ditches in 1923 and the salination of water lines), the quantity of water resulting in the wetland had been limited (Figure 6). Moreover, the abstractions and the alteration of the hydrologic regime from the draining channels, led to the gradual extinction of small habitats of the area and mainly of the seasonal ponds. The coastal pine forest (one of the few remaining in the Mediterranean) is located between the wetland and the sea, on a sandy area with dunes and is one of the three pine forests in Greece. The stone pines or umbrella pines (Pinus pinea) with the characteristic crown-like umbrella, spread mainly on the west of the forest, while to the east, it coexists with aleppo pine (Pinus halepensis), which gradually replace it. The forest covers area of about 3.5km on a sandy strip about 400m wide and presents a lowland character. The slopes are smooth, 0-2%, and only the sandy coastal zone presents a higher inclination towards the sea [11].





Figures 5&6: Schinias Olympic Rowing and Canoeing Centre, in the National Park of Schinias-Marathon (Fig. 5)(Source of aerial photos: TripInView/Geotag Aeroview 2014). Marathon water supply dam and artificial lake (1AttiArtL) (Fig. 6, Photo by Asimina Mertzani).

It should be noted that most the names of fragile aquatic ecosystems and water resources and wetlands and all the codes (e.g. 1AttiWETL) have been given by the study group for the studied areas. These codes are combinations of letters and numbers. The number represents the scenting number of the relevant category (e.g. 1). The letters represent the initials of the prefectures' name (e.g. Atti=Attica). The end of the code represents the initials of these aquatic resources and wetlands (e.g. WETL= Wetland).

2.2 Study methodology

For the depiction of the environmental situation of the depiction of the environmental situation of the fragile aquatic ecosystems and water resources (wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes) of Attica region, involved a series of different stages: the study of bibliographical references, systematic in situ observations (field-work), measurements using the Global Positioning System (GPS) satellite signals, observation and direct digitizing on the basis of different aged aerial photos (TripInView) and satellite images (Landsat, Google Earth) [12]. For the assessment and evaluation of the impact caused by certain human activities to the environment and geomorphology of the areas under study and especially, to the hydro-geomorphological processes in the coastal zones, shorelines, lagoons, deltas, lakes, ponds, marshes, wetlands and watersheds, have been used aerial photos various years and scale as well as satellite images [12]. The "in situ" observations were conducted, at least, every 5 years during the months of April, July, October and January for the years 1996, 2001, 2006, 2011 and 2016, in selected places of each aquatic

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ecosystem under study. All primary data were imported in an apposite database and were transferred in topographical map and onto satellite images. Thus the database was developed and updated with data deriving from different sources. Data were analyzed quantitative and qualitative, while apposite thematic checklists, cumulative charts and tables were created.

3. RESULTS - DISCUSSION

3.1 Anthropogenic pressures on the fragile aquatic ecosystems and water resources of Attica region - Environmental impacts

Anthropogenic pressures and interventions in the areas under study, had different aims in each location, but all of them resulted in the disruption of the natural environment and alteration of the dynamic evolution of the hydro-geomorphological processes, leading to the creation of an “artificial” environment, controlled to a considerable extend by humans. The possibility of environmental destabilization is re-strengthened and re-enforced in the long run [13,14,15,3,1,4,5,16]. Unfortunately, most of the fragile aquatic ecosystems and water resources of Attica region are being degraded and are under imminent threat by multiple human-induced pressures (Figures 7,8,10,11,12,14&15). The main anthropogenic degradation and stresses on these ecosystems includes wetland draining, intensification and development of agriculture projects, river engineering works, hydroelectric dams, water pollution, holiday home building, and uncontrolled water abstraction from surface & underground water tables.





Figures 7&8: Asopos river delta-estuaries (1AttiWETL) near Halkoutsi (Fig. 7) and Artemida marsh (Loutsa)(5AttiWETL) in Artemida (Fig. 8) at South Euboean gulf (Source of aerial photos: TripInView/Geotag Aeroview 2014). The main anthropogenic degradation and stresses on these ecosystems includes wetland draining, intensification and development of agriculture projects, river engineering works, water pollution, holiday home building, and uncontrolled water abstraction.

The intensification of multiple anthropogenic pressures and interventions in recent decades in the river mouths, deltas and lagoons and in the drainage basin of its rivers has affected the natural ecosystems, especially degrading sensitive wetland habitats [4,5,16]. The construction and operation of the Marathon water supply dam in the drainage basin of Inois river (or Haradros) and “Rapentosa” flood control dam, in the Rapentosa basin, may seriously affect the environmental balance of wetlands in the river mouth areas (Figures 6&11). The most common man-made changes on the natural environment of the delta areas, river mouths, marshes, lagoons and lakes, under study, are: a. Alterations to the fauna, the flora and the local natural ecosystems, b. Landscape changes, c. Alterations to the surface and underground waters and c. Alterations on the geological-geomorphological features and the hydro-geomorphological processes.

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Below there are presented the cumulative chart of the anthropogenic pressures and interventions that stress the fragile aquatic ecosystems and water resources (wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes) of Attica region (Figure 9). This Cumulative chart serves as a "tool" for the reduction of manmade eco-environmental impact on the wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes in Attica region and the rational environmental management of these fragile aquatic ecosystems and water resources, offering an overall visualization of the pressures/impact, in order to protect the function and value of wetlands.

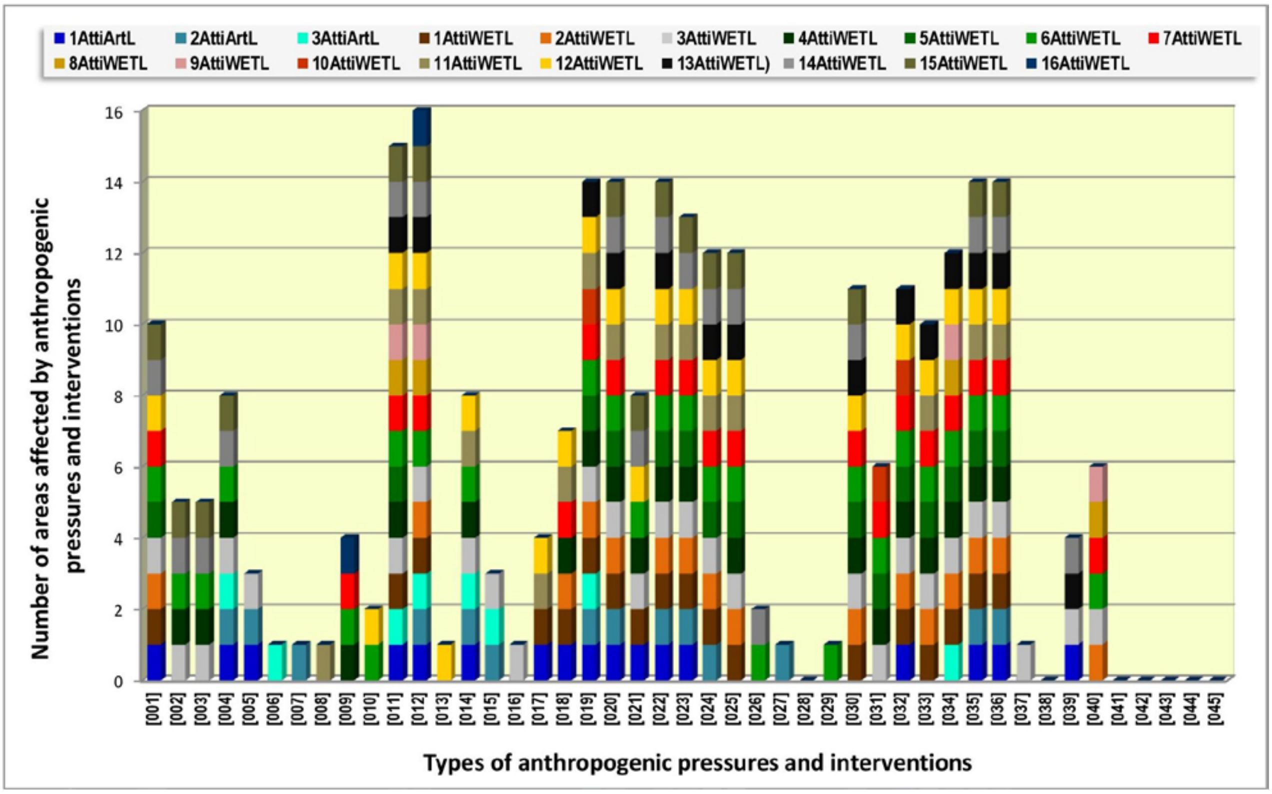


Figure 9. Cumulative chart of the anthropogenic pressures and interventions that stress the fragile aquatic ecosystems and water resources of Attica region

It should be noted that in the cumulative chart of Figure 9, each one of the anthropogenic pressures and interventions that stress the fragile aquatic ecosystems and water resources of Attica region receive one point. The legend of Figure 9 are: [001]. Intensification and development of agriculture, [002]. Construction of irrigation channels and drainage pits, [003]. Deepening and creation of channels, [004]. Construction of drainage - anti flooding protection works, [005]. Construction and function of large dams and reservoirs (hydroelectric power dams, irrigation dams and water supply dams) on the main bed of the river (>15.0 m height or reservoir volume > 3.0 million m^3), [006]. Construction and function of large dams and reservoirs (hydroelectric power dams, irrigation dams and water supply dams) on tributaries of major river (>15.0 m height or reservoir volume > 3.0 million m^3), [007]. Intense construction of anti-erosion works in mountainous catchment basins (small dams, etc.), [008]. Intense construction of coastal defence management schemes (seawalls, breakwaters, groins, revetments, rock armour, gabions, beach replenishment, sand dune stabilization, etc.), [009]. Construction of jetties in the coastal zone, [010]. Motorway in operation or under construction, [011]. National or provincial roads in operation or under construction, [012]. Opening up new agricultural and forest roads, [013]. Railway line in operation or under construction, [014]. Infrastructure works, [015]. Wood cutting, intense deforestation/Forest fires, [016]. Intense deforestation of riparian vegetation, [017]. Industrial activities upstream, [018]. Small business activities upstream, [019]. Urban and industrial development without any planning, [020]. Uncontrolled deposition of urban waste, industrial effluents, solid domestic and industrial waste, [021]. Excessive use of pesticides and fertilizers, [022]. Contamination-pollution (water & soil pollution, etc.), [023]. Alteration of the physicochemical characteristics - deterioration of the quality of water (salinity, etc.), [024]. Embankment-filling of lagoons or lakes with sediment, [025]. Drain of marshes, lakes lagoons/Exsiccation-desiccation of marshes and lakes, [026]. Canal shifting and entrenchment of the main river channels/river diversion

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projects, [027]. Intense mining activities (quarries, mines)/in upstream, [028]. Sand and gravel extraction from river beds (in upstream), [029]. Uncontrolled watering from surface water tables, [030]. Uncontrolled pumping of underground waters, [031]. Mass touristic activities, recreation, [032]. Domestic use, [033]. Intense urbanization of large coastal zones with impacts on the natural environment and the local natural ecosystems, [034]. Holiday home building, [035]. Sources of water pollution/in upstream, [036]. Solid wastes/Rubbish water pollution, [037]. Grazing in the forest, [038]. Overgrazing, [039]. Hunting-poaching, [040]. Various off-road 4x4 and motocross races, [041]. Use of lagoons or lakes for fishery, water cultivations, [042]. Coastal farming - Fish farming in coastal waters <500 m from shore and <10 m water depth, [043]. Coastal farming - Fish farming in coastal waters <500 m from shore and >10 m water depth, [044]. Off-coast farming - Fish farming in coastal waters 500 m to 3 Km from shore and 10 to 50 m water depth, [045]. Use of lagoons for salt production.

The identification, recording and evaluation of the multiple anthropogenic pressures and interventions that have been encountered as of now in the fragile aquatic ecosystems and water resources of Attica region, are summarized in Figure 9. The most important once are the following, in decreasing order: “Opening up new agricultural and forest roads-Code 12”, “National or provincial roads/in operation or under construction-Code 11”, “Urban and industrial development without any planning-Code 19”, “Uncontrolled deposition of urban waste, industrial effluents, solid domestic and industrial waste-Code 20”, “Contamination-pollution (water & soil pollution, etc.)-Code 22”, “Sources of water pollution in upstream-Code 35” and “Solid wastes/Rubbish water pollution-Code 36” (Figure 9).



Figures 10&11: National Park of Schinias-Marathon. The large number of bathers and uncontrolled car parking in the pine forest and sand dunes of the protected area, constitutes type of pressure on the natural environment (Fig. 10). The remains of roots of pine trees bear witness to the erosion phenomena and regression of the shoreline (Fig. 11)(Photos by Asimina Mertzani)

Until the beginning of the 20th century, natural processes control the evolution of the Marathon plain, whilst afterwards, they are of less importance due to increasing human activities. During the last decades, a rapid expansion of constructing activities; buildings, roads, bridges, irrigation network, etc; reduces the wetlands and not-cultivated areas; pin-tree forest of Schinias, Drakonera lake, Marathon marsh [9]. Dune field in places has been abused by human activities; mainly due to building development (Figures 4,5&10).

The marine part of the shore zone as the rest of the Marathon gulf floor used to receive the water/sediment influx of the Inois river (Haradros river) that drains an area of 177.2 km^2 before the construction of the Marathonas dam. The wave energy is dissipated due to shallow bathymetry creating weak longshore currents that usually are not capable to initiate sediment transport [10]. On the main river channel of Inois has built and operates the Marathon water supply dam. The construction of this dam was completed in 1929. The surface of the artificial lake is about 2.45 km^2

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at full supply level. As a result, the Inois riverbed has presented significant changes to its network shape. In addition, a significant retreat of the shoreline (~100 m) near the Inois (Haradros) river mouth during the last 120 years, may be caused mainly by: 1. the drastic reduction of riverine sediment supply due to the construction of the Marathon dam, in 1929; and 2. The sand extraction from the lower course of the riverbed [9]. Erosion in this coastal zone is still active, and in spite of the presence of some protection measures (i.e. sea walls, artificial nourishment), the erosion rate is likely to increase because of the prospective rise of the sea level [6,7,8,9] (Figure 11). Currently, erosional phenomena have been observed to the south of the mouth of river Inois, whilst to its northern part not significant changes have been recognized so far [10]. According to Poulos et al. (2004) the human interference is related to: a. the construction of the Marathonas dam that basically inhibits fluvial sediment to reach the coast, b. coastal development plans, including the constructions for the Olympic Games of 2004 and c. several constructions related to the shore zone and the associated dune-field [10].




Figures 12&13: Vouliagmeni lake (10AttiWETL) southeastern of Vouliagmeni (Fig. 12) and Anavyssos lagoon (8AttiWETL) southwestern of Anavyssos (Fig. 13), at Saronikos gulf (Source of aerial photos: TripInView/Geotag Aeroview 2014).

An important role in the eco-environmental impacts and geomorphological evolution of dynamic coastal areas and wetlands (river mouths, deltas and lagoons), seems to play the climate change with the subsequent “sea level rise”. One of the consequences of the global climatic change is the loss of coastal land, coastal wetlands, deltas, lagoons and marshes (inland and coastal environments), which are important for their environmental and economic values, due to a potential sea level rise; on a global scale, the latter has been predicted to be in between 38 and 68 cm for the year 2100, according to the latest report by the IPCC [17]. The future regression of the shoreline, primarily caused by the climate change and the rising sea level, is expected to affect harshly the low lying coastal areas (Figures 1,2,3,4,7,8,11,13,14&15).




Figures 14&15: Oropos lagoon (2AttiWETL), near Ag. Konstantinos and northeastern of Halkoutsi at South Euboean gulf. The future regression of the shoreline, is expected to affect harshly the low lying coastal areas, such as those in the pictures (Source of aerial photos: TripInView/Geotag Aeroview 2014).

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3.2 Strategy for the mitigation of the manmade eco-environmental impact

For the rational environmental management of the fragile aquatic ecosystems and water resources of Attica region in order to address the environmental impact of projects and activities and in order to restore gradually the disturbed balance of affected natural ecosystems, many measures have to be taken. These include the use of specialized environmental protection measures, strict control and monitoring of these measures and the safeguarding of the boundaries of protected areas. The main protective measures listed below, are: 1. Detailed surveying, identification and high spatial resolution mapping of the fragile aquatic ecosystems and water resources under study, 2. Comprehensive study of all habitats in the different sites of Attica region, 3. Comprehensive study of the geological, geomorphological and hydrogeological characteristics of the areas under investigation, such us the wetlands, deltas, estuaries, lakes, ponds, lagoons and marshes that exist in Attica region, 4. Reduction of pollutant emissions and more generally of the environmental impact of the different anthropogenic pressures and interventions, 5. Reevaluation of locating the different anthropogenic pressures and interventions under study and taking adequate measures, 6. Reevaluation of the operation of treatment plants of urban waste water and taking adequate measures, 7. Reevaluation of the operation of industrial wastewater treatment plants and livestock installations and taking adequate measures, 8. Reevaluation of the operation of industrial and manufacturing installations wastewater treatment plants as well as livestock installations and taking adequate measures, 9. Reduction of gaseous pollutant emissions and aerosols, 10. Implementation of municipal solid waste management projects, 11. Implementation of projects on waste management and recycling, 12. Implementation of hazardous and toxic waste management projects, 13. Implementation of water saving programs in irrigation and industrial production, 14. Reduction of fertilizers, herbicides, and pesticides in agricultural production, 15. Implementation of ecosystem restoration project for improving and increasing aquatic and terrestrial habitats and ecological function in the lakes, lagoons, deltas and its tributaries. The “Ecosystem Restoration Program” is guided by the following six strategic goals [18]: a. Recover endangered and other at-risk species and native biotic communities, b. Rehabilitate ecological processes, c. Maintain or enhance harvested species populations, d. Protect and restore habitats, e. Prevent the establishment of and reduce impacts from non-native invasive species, and f. Improve or maintain water and sediment quality, 16. Multi-temporal monitoring of the broader area of the fragile aquatic ecosystems and water resources under study.

4. CONCLUSIONS

The intensification of multiple anthropogenic pressures and interventions in recent decades in the wetlands, lakes, lagoons and marshes of Attica region and in the drainage basin of its rivers and streams, has affected the natural ecosystems, especially degrading sensitive wetland habitats. The main anthropogenic degradation and stresses on these ecosystems includes wetland draining, intensification and development of agriculture projects, river engineering works, water supply dams, water pollution, holiday home building, and uncontrolled water abstraction from surface and underground water tables. Sprawling urban areas are also located in and near the lowland plains of these wetlands.

The identification of anthropogenic pressures that stress the natural environment and specifically the deltaic ecosystems in combination with the proper assessment and evaluation of the impact, constitute part of the necessary strategic conservation planning and monitoring procedure. This is a baseline requirement for informing relevant management bodies in order to implement protection and restoration actions and foster sustainability in these biodiversity-rich areas.

The appropriate design and the application of methods and techniques for the management of the fragile aquatic ecosystems and water resources is a condition for the preservation of the

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equilibrium of the natural hydrological and geomorphological processes, the renewal of the natural resources and, in general, environmental protection.

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References

[1] Mertzanis A, Goudelis G, Efthimiou G and Kontogianni A (2010). The impact to the environment and the hydro-geomorphological processes as a result of human activity in littoral and inland wetlands in Greece. *Proceedings of the International Conference Protection and Restoration of the environment X*, 05 – 09 July 2010, Corfu, Greece.

[2] United States Environmental Protection Agency (U.S. E.P.A.). (2001). *Treats to wetlands*. EPA 843-F-01-002d, September 2001.

[3] Vavizos, G., Mertzanis, A., 2003. *Environment-Studies of Environmental Impact*. Papasotiriou, Athens. pp. 342. (in Greek).

[4] Kousouris, Th., (2014). *The lakes in Greece. 2/6. Epirus. "Lakes recordings & Testimonials"*, Athens. pp. 73. (in Greek).

[5] Kousouris, Th., (2016). *The small lakes in Greece. "Small lakes images and tours"*, Athens. pp. 498. (in Greek).

[6] Maroukian H, Pavlopoulos K, Zamani A. Coastal retreat in the plain of Marathon (East Attica) Greece: Causes and effects. *Geologica Balcanica*. 1993;**23**(2):67-71.

[7] Pavlopoulos K, Karympalis E, Maroukian H. Geomorphological evolution of Inois river drainage basin (N. Attica) in the Quaternary. *Proceedings 6th Panhellenic Geographical Congress*, Thessaloniki, Greece. 2002; Vol. 1. (in Greek).

[8] Pavlopoulos K, Karkanas P, Triantaphyllou M, Karympalis E, Tsourou Th, Palyvos N. Paleoenvironmental evolution of the coastal plain of Marathon, Greece, during the Late Holocene: Depositional Environment, Climate, and Sea Level Changes. *Journal of Coastal Research*. 2006;**22**(2):424-438. (in Greek).

[9] Seni A, Kapsimalis V, Pavlopoulos K. Determination of recent geomorphologic changes in the Marathon coastal plain (Attica, Greece), using geographical information systems. *Proceedings 7th Panhellenic Geographical Congress*, Mytilini, Greece. 2004. (in Greek).

[10] Poulos S, Iordanis K, Gourdoubas I, Pavlopoulos K. The sedimentary environment of the shore zone of the Sxinias Bay (Marathonas Gulf). *Proceedings 7th Panhellenic Geographical Congress*, Mytilini, Greece. 2004; 238-245. (in Greek).

[11] Management Board of Schinias Marathon National Park. "National Park of Schinias Marathon". Retrieved from http://www.npschiniasmarathon.gr on 09 May 2016.

[12] TripInView. Retrieved from http://www.tripinview.com/en?path=home on 28 April 2016.

[13] Brofas G., (1989). The restoration of vegetation at the land mines. *Conference GEOTEE*, 12-13 April, Athens. (in Greek).

[14] Zalidis HG, Matzavelas AL. *Inventory of the Hellenic Wetlands as Natural Resources*, G.B.W.C.-XVII, p.587; 1994. (in Greek).

[15] Dafis S, Papastergiadou E, Georgiou K, Babalonas D, Georgiadis D, Papageorgiou M, et al. (1997). *Directive 92/43/EEC. Wetlands works in Greece: Network Natura 2000*. Contract. B4-3200/84/756, General Directorate XI Commission of the European Communities, The Goulandri Natural History Museum, G.B.W.C. 932 p; 1997. (in Greek).

[16] Greek Biotope-Wetland Centre (EKBY)/Region of Attica. (2014). *Vulnerability assessment of wetlands in Attica of climate change and action plan*. Athens. pp. 124. (in Greek).

[17] Intergovernmental Panel on Climate Change (IPCC) (2007). *Climate Change 2007: Impacts, Adaptation and Vulnerability, Working Group II Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der Linden, C.E. Hanson, Eds. Cambridge Univ. Press, Cambridge, UK, 976 pp., 2008.

[18] California Department of Fish and Wildlife. "Ecosystem Restoration Program", www.wildlife.ca.gov Retrieved from http://www.dfg.ca.gov/erp/ on 27 April 2016.

Evaluation of soil water diffusivity using different methods from horizontal absorption

C. Evangelides[1*], G. Arampatzis[2], C. Tzimopoulos[1]

[1]Department of Hydraulics and Transportation Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
[2]Soil and Water Resources Institute, Hellenic Agricultural Organisation-DEMETER, 57400 Sindos, Greece.
*Corresponding author: Email: evan@vergina.eng.auth.gr

Abstract

Diffusivity is one of the main soil hydraulic properties. It is a critical parameter for the prediction of water transport within the vadoze zone. The aim of this paper was to establish the soil water diffusivity of a soil sample utilizing two experimental methods. The first method uses gamma ray measurements for the soil moisture. It utilized the proposed method by Whisler et al (1968), which requires knowledge of the complete soil moisture profile at certain distances from the beginning of the soil column. It is different than the one proposed by Bruce and Clute (1956), which requires knowledge of the entire soil profile at discrete times, which presents many difficulties during experiments especially when there is only one instrument available for soil water moisture measurements. The second method uses profile length observations, sorptivity, initial and final moisture content. The objective is to use a complex empirical function with three constants to generate the transformed soil moisture profile by treating the process as an optimization problem. The required conditions to compute the constants of the empirical function are: a) the analytically computed sorptivity should agree with the experimental one, and b) the beginning and the end of the transformed soil moisture profile should agree with the final and the initial water content correspondingly. Once an analytic function for the transformed soil moisture profile is determined, then diffusivity is calculated analytically. Integral continuity is preserved throughout the process. Both methods were verified using the water volume absorbed during the horizontal experiment and the results were very satisfactory.

Keywords: *diffusivity; soil water properties; horizontal absorption*

1. INTRODUCTION

Soil hydraulic properties are very important in the prediction of water flow. The necessary properties are hydraulic conductivity, diffusivity and specific capacity (Bohne et al., 1995). Measurement of these properties is complex, time consuming and requires quite expensive instruments.

Recently there is a tendency to consider soil water diffusivities of unsaturated soils as one significant soil hydraulic property. A method for measuring hydraulic conductivity and soil water diffusivity was described initially by Gardner (1956) using pressure plate outflow data. Bruce and Clute (1956) utilized horizontal absorption to relate soil water diffusivity to the volumetric water content. Their method is based on the Boltzman (1894) transformation and measurements of the water content slope distribution curve along the soil column. Since accurate determination of the slope is very difficult, errors arise also in the determination of soil water diffusivity. Whisler et al (1968) introduced a method that used the same theoretical analysis as that in the Bruce and Clute (1956) method, but the diffusivity is based on the water distribution as a function of time at a fixed position instead of the water content distribution with distance at a specific time. Clothier et al. (1983) utilized a fitting function from the ones proposed by Phillip (1960) to approximate the water

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content distribution curve. This led to an analytical function for the description of the water diffusivity, but this function may not apply to all soil types. McBride and Horton (1985) developed a method of determining water diffusivity using an empirical fitting function for the soil moisture profile from horizontal absorption experiments, but require cumbersome calculations. Shao and Horton (1996) developed a method to estimate soil water diffusivity by using an analytical solution to horizontal redistribution based on general similarity theory. They assumed a power function relationship between soil water diffusivity and soil water content, which may not apply to all soil types. Šimůnek et al. (2000) used a parameter estimation approach to analyze horizontal infiltration data to obtain the diffusivity water content function. They utilize numerical inversion in order to gain additional information about the water retention curve and the hydraulic conductivity function. Wang et al. (2002) presented an analytical method to determine Brooks – Corey model parameters from horizontal infiltration. Wang et al. (2004) utilized cumulative infiltration, infiltration rate and wetting front distance in order to estimate the soil water diffusivity. However the assumption is a good approximation only when soil water content is close to saturation and so far limited number of soils has been used to test the assumption. Ma et al. (2009) developed an analytical method for estimating soil hydraulic parameters and they tested their method on nineteen numerical soils and not experimental data. They used the assumption of exponential flux distribution to determine Brooks and Corey model parameters. They utilized an experimentally revised shape coefficient to guarantee agreement of water content, soil tension, water flux distribution and cumulative infiltration estimated by the analytical method with those calculated by HYDRUS-1D software.

The aim of this paper was to establish the soil water diffusivity of a soil sample utilizing two experimental methods. The first method uses gamma ray measurements for the soil moisture. It utilized the proposed method by Whisler et al (1968), which requires knowledge of the complete soil moisture profile at certain distances from the beginning of the soil column. It is different than the one proposed by Bruce and Clute (1956), which requires knowledge of the entire soil profile at discrete times, which presents many difficulties during experiments especially, when there is only one instrument available for soil water moisture measurements. The second method uses profile length observations, sorptivity, initial and final moisture content. The objective is to use a complex empirical function with three constants to generate the transformed soil moisture profile by treating the process as an optimization problem (Evangelides et al. 2010) and finally to extract the diffusivity coefficient directly from the transformed soil moisture profile.

2. THEORY

The one dimensional horizontal movement of water in unsaturated soil can be described by the equation (Bruce and Clute, 1956 and Whisler et al., 1968):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left[D(\theta_x)\frac{\partial\theta}{\partial x}\right] \qquad 0 < x < \infty \tag{1}$$

where θ is the water content (L^3L^{-3}), D is the diffusivity (L^2T^{-1}), x is the position (L), and t is time (T). Equation 1 implies that Darcy's law is valid for unsaturated flow, whereas it is assumed that a unique relationship exists between the pressure head and the water content (Nielsen et al., 1962). The initial and boundary conditions for horizontal absorption are:

$$\begin{aligned} \theta(x,t) &= \theta_i \qquad && x \geq 0,\ t = 0 \\ \theta(x,t) &= \theta_0 && x = 0,\ t > 0 \\ \theta(x,t) &= \theta_i && x \to \infty,\ t > 0 \end{aligned} \tag{2}$$

where θ_i is the initial water content (L^3L^{-3}) and θ_0 is the final water content (L^3L^{-3}).

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By introducing the Boltzman transformation $\lambda = x\, t^{-1/2}$, which assumes that the water content θ_x is a single valued function of λ, Equation (1) is transformed into the ordinary differential equation:

$$-\frac{1}{2}\lambda\frac{d\theta}{d\lambda} = \frac{d}{d\lambda}\left[D(\theta_x)\frac{d\theta}{d\lambda}\right] \tag{3}$$

with the following boundary conditions:

$$\theta_x = \theta_i \qquad \lambda \rightarrow \infty$$
$$\theta_x = \theta_0 \qquad \lambda = 0$$

Integrating Equation 3 between the limits θ_i and θ_x yields:

$$D(\theta_x) = -\frac{1}{2}\frac{1}{\left(\frac{d\theta}{d\lambda}\right)_{\theta_x}}\int_{\theta_i}^{\theta_x}\lambda\, d\theta \tag{4}$$

According to Philip (1969), sorptivity (S) is given as:

$$S = \int_{\theta_i}^{\theta_0}\lambda\ d\theta \tag{5}$$

The cumulative infiltration (I) to the wetting front can be expressed as:

$$I = \int_{\theta_i}^{\theta_0} x\ d\theta \tag{6}$$

Equations 5 and 6, using Boltzman transformation, become:

$$S = \frac{I}{\sqrt{t}} \tag{7}$$

Assuming an empirical function with three constants (a, b and c) for the transformed soil moisture profile:

$$\theta(\lambda) = -\left[\theta_0 + a\tan^{-1}(b\ \lambda + c)\right] \tag{8}$$

or

$$\lambda(\theta) = \frac{1}{b}\left[\tan\left(-\frac{\theta+\theta_0}{a}\right) - c\right] \tag{9}$$

The Equation 8 and 9 have similar form to the one proposed by Evangelides et al. (2005) for the transformed soil moisture profile, but with three constants instead of four.

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Sorptivity (Equation 5) using Equation 9 becomes:

$$S = \int_{\theta_i}^{\theta_0} \lambda \, d\theta = -\frac{c}{b}(\theta_0 - \theta_i) + \frac{a}{b} \ln\left(\frac{\left|\cos\frac{2\theta_0}{a}\right|}{\left|\cos\frac{\theta_i + \theta_0}{a}\right|} \right) \quad (10)$$

Diffusivity (Equation 4) as a function of θ using Equation (9) becomes:

$$D(\theta_x) = -\frac{1}{2} \frac{1}{\left(\frac{d\theta}{d\lambda}\right)_{\theta_x}} \int_{\theta_i}^{\theta_x} \lambda \, d\theta =$$

$$= -0.5 \frac{1 + \left(\tan\left(-\frac{\theta_x + \theta_0}{a}\right)\right)^2}{a \; b} \left[\frac{c}{b}(\theta_x - \theta_i) + \frac{a}{b} \ln\left(\frac{\left|\cos\frac{\theta_i + \theta_0}{a}\right|}{\left|\cos\frac{\theta_x + \theta_0}{a}\right|} \right) \right] \quad (11)$$

which gives diffusivity analytically at any θ_x between θ_i and θ_0, once a, b and c are determined.

3. MATERIALS AND METHODS

The physical problem was studied in the laboratory using a plexiglass cylindrical column, 100 cm long, 6 cm inside diameter, and placed horizontally. The bulk densities and the moisture content were measured by γ-ray absorption method (Davidson et al., 1963; Reginato and van Babel, 1964; Vachaud and Thony, 1971). The device of γ-ray contained a 300 mCi Americium –241 source. The Americium source and the photomultiplier detector (including a NaI crystal and preamplifier) were set on a platform connected to a stepper motor. In this way one can follow the development of water profiles in the column over time.

Soil sample was filtered through a 1 mm sieve in order to remove foreign particles, dried in 105^o C for 24 hours and crumbled. Then it was packed in a transparent plexiglas column with 100 cm length and 6 cm inside diameter

The soil sample was graded from 0.425 to 0.6 mm in order to be homogeneous. The column was packed using a soil placement method with free-failing soil passing through a sequence of sieves. With this method, a good homogeneity of sand packing can be achieved. The soil column had a mean bulk density of 1.593±0.015 g/cm^3 and was 100 cm high. All experiments were carried out at a constant temperature of 21 ± 1^oC. Measurements were also obtained for saturated moisture content θ_s=0.385 cm^3/cm^3, the residual moisture content which is equal to the initial moisture content θ_r = 0.006 cm^3/cm^3. The experimental setup is shown in Figure 1.

Water was applied at the initial time t = 0 to the one end of the sample (x=0) under zero constant-head in order to obtain boundary condition θ_0=θs. A fine plastic screen was used at both ends of the column, in order to prevent the soil from dispersing during the experiment. The water pressure entering the column was controlled by a Mariotte burette, which was connected to the column by means of a transparent plastic tube. Continuous monitoring of the water entering the column was possible since the Mariotte burette was placed on an electronic digital scale. Water content, as a function of time, was measured by scanning the column with gamma rays (Davidson et al., 1963; Reginato and van Babel, 1964) at positions 11.3, 33.3 and 52.3 cm from the beginning of soil column (Whisler, 1968). Wetting front distance with time was also observed visually based on obvious color differences at the interface of wet and dry soil (Evangelides et al., 2010). Saturated

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water content was measured volumetrically after the end of the horizontal absorption by continuing the wetting process in a vertical position until saturation.

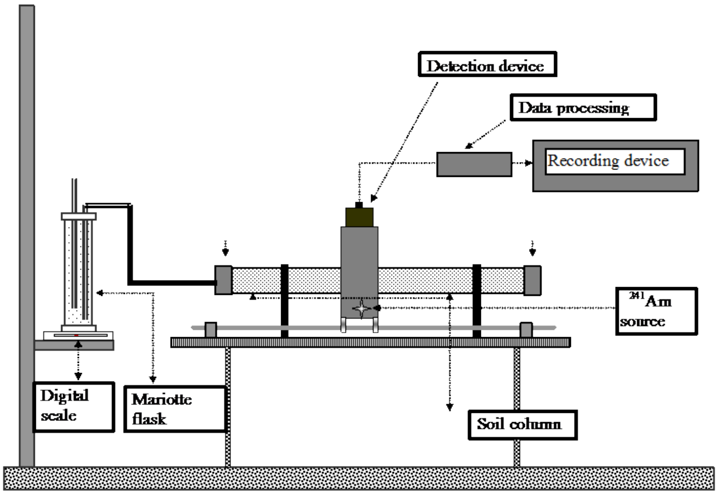


Figure 1. Horizontal soil column.

4. RESULTS AND DISCUSSION

The transformed profile was determined from the γ-ray measurements of soil moisture versus time in the three predefined positions. This experimental profile was fitted with the generalized Equation 9 and the three constants were determined, as shown in Figure 2 with an Relative Mean Square Error (R.M.S.E.) of 1.5E-02 and a correlation coefficient of 0.9. Using the three constants and Equation 11 D(θ) was determined analytically (Figure 4).

At the visual method, cumulative infiltration was calculated from the volume of the absorbed water and the cross section of the column at the end of profile lengths on specific times. Consequently from the calculated infiltration, and the time that profile arrived at a certain position Equation 7, sorptivity was calculated. Finally the transformed profile length was calculated through Boltzman transformation. The results of this procedure are presented in Table 1 and Figure 3.

Table 1. Values obtained through the visual experimental process.

t(min)	I(cm)	S(cm/min$^{0.5}$)	$X_{profile}$(cm)	λ(cm/min$^{0.5}$)
0.00	0.0000		0	
2.20	6.1290	4.1322	24	16.1808
7.00	11.0163	4.1638	42	15.8745
9.40	12.6869	4.1380	49	15.9820
16.30	16.7589	4.1510	65	16.0998
20.00	18.5561	4.1493	72	16.0997
Average		4.1468		16.0474

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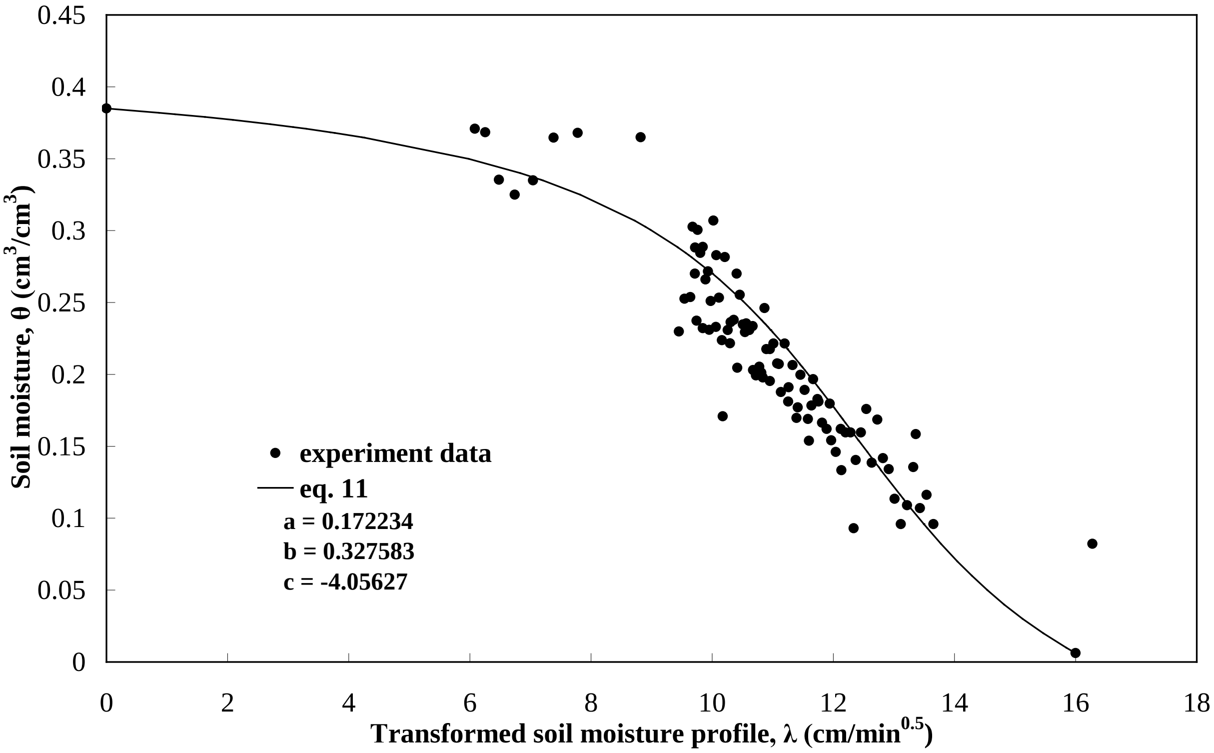


Figure 2. Experimental points obtained with γ-ray and fitted profile.

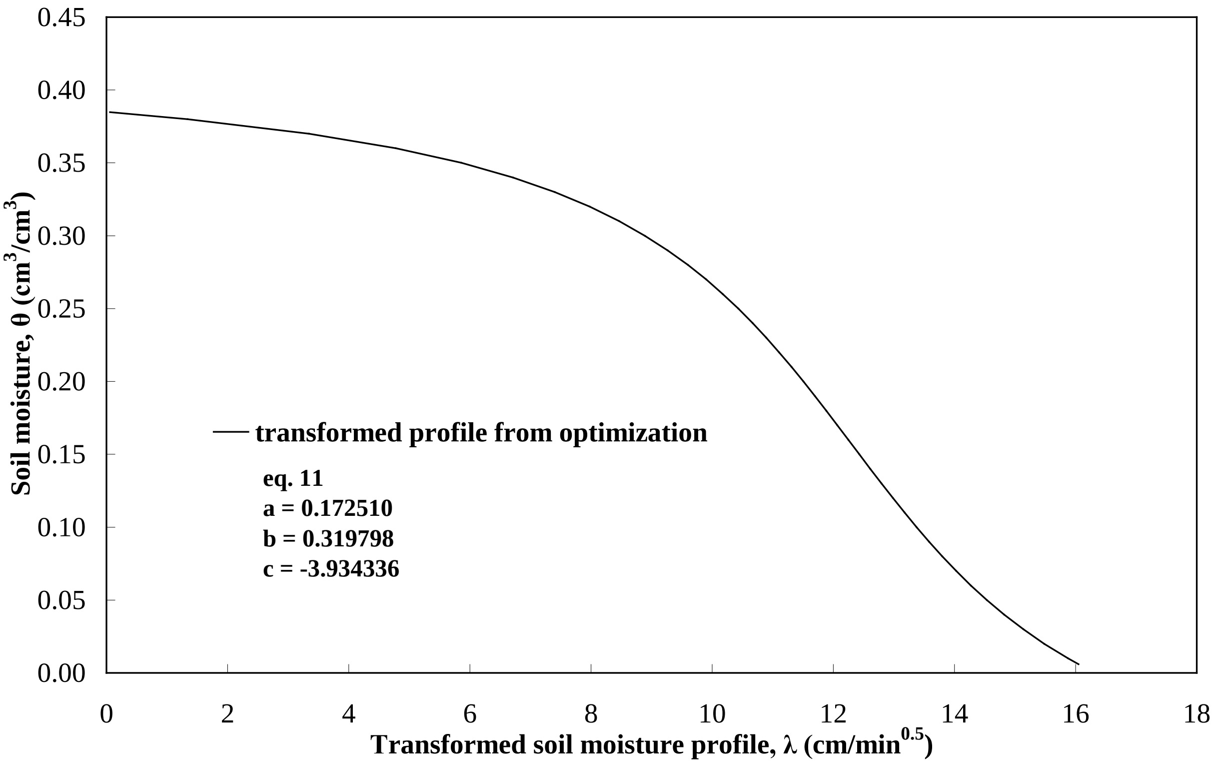


Figure 3. Experimental points obtained with visual method and fitted profile.

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Using the values of the sorptivity of the visual inspection, initial and final moisture content in Equation 9 the transformed profile was generated through optimization process using conjugate directions. Using the three constants and Equation 11 D(θ) was determined analytically for the visual process (Figure 4).

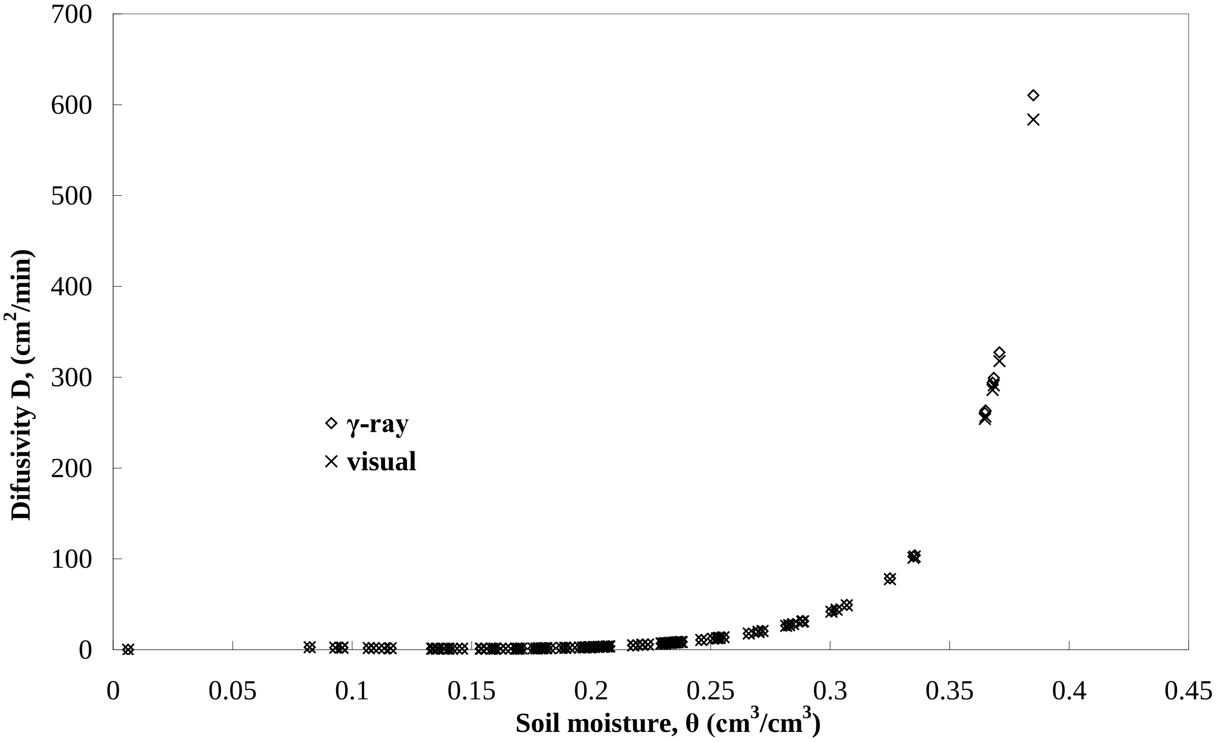


Figure 4. Difissuvity

5. CONCLUSIONS

The original Bruce and Clute method requires knowledge of the soil moisture profile during horizontal absorption of the whole sample at different times. This was feasible, because moisture content was measured volumetrically after sectioning the soil column. On the contrary nowadays since there are limited moisture measuring devices, it is preferable to measure a whole profile in specific positions. In this article this method is compared with a visual method that was developed by our laboratory during a horizontal experiment.

The advantages of the described visual method is that there is no need to measure soil moisture since the transformed wetting profile is recreated from visual distance measurements, water volume measurements and optimization. Consequently, there is no need for expensive equipment.

The results show that there is a very satisfactory agreement in establishing the diffusion coefficient between the two methods providing that the wetting profile is sufficiently visible. The diffusivity was found to be 610 cm^2/min with the γ ray method while was 584 cm^2/min with the visual method. Additionally, the correlation coefficient between the two methods was found to be 0.999.

References

[1] Bohne K., Roth C., Leij F.J. and van Genuchten M. Th., 1995. Rapid method for estimating the unsaturated hydraulic conductivity from infiltration measurements. *Soil Science*, 155, 237-244.

[2] Boltzman L., 1894. Zur integration der diffusionsgleichung bei variablen diffusion koeffizienten. *Annalen der Physik and Chemie*, 53, 959-964.

ISBN: 978-960-6865-94-7

[3] Bruce R.R. and Klute A., 1956. The measurements of soil moisture diffusivity. *Soil Science Society of America Proceedings*, 20, 458-462.
[4] Clothier B.E., Scotter R.D. and Green E.A., 1983. Diffusivity and one dimensional absorption experiments. *Soil Science Society of America*, 47, 641-644.
[5] Davidson J.M., Biggar D.W. and Nielsen D.R., 1963. Gamma – radiation attenuation for measuring bulk density and transient flow in porous media. *Geophysical Research*, 68, 4777 – 4783.
[6] Evangelides C., Tzimopoulos C. and Arampatzis G., 2005. Flux-saturation relationship for unsaturated horizontal flow. *Soil Science*, 170, 671-679.
[7] Evangelides C., Arampatzis G. and Tzimopoulos C., 2010. Estimation of Soil Moisture Profile and Diffusivity Using Simple Laboratory Procedures. *Soil Science*, 175(3), 118-127.
[8] Gardner W.R., 1956. Calculation of capillary conductivity from pressure plate outflow data. *Soil Science Society of America Proceedings*, 20, 317-320.
[9] Ma D., Wang Q. and Shao M., 2009. Analytical method for estimating soil hydraulic parameters from horizontal absorption. *Soil Science Society of America*, 73, 727-736.
[10] McBride J.F. and Horton R., 1985. An empirical function to describe measured water distributions from horizontal infiltration experiments. *Water Resources Research*, 21, 1539-1544.
[11] Nielsen R.D., Biggar W.J. and Davidson M.J., 1962. Experimental consideration of diffusion analysis in unsaturated flow problems. *Soil Science Society of America*, 26, 107-111.
[12] Philip J.R., 1960. General method of exact solutions of the concentration-dependent diffusion equation. *Australian Journal of Physics*, 13, 1-12.
[13] Reginato R.J. and van Babel C.H.M., 1964. Soil water measurement with gamma attenuation. *Soil Science Society of America Proceedings*, 28, 721 – 724.
[14] Shao M. and Horton R., 1996. Soil water diffusivity determination by general similarity theory. *Soil Science*, 161, 727-734.
[15] Šimůnek J., Hopmans J., Nielsen D. and van Genuchten Th., 2000. Horizontal infiltration revisited using parameter estimation. *Soil Science*, 165, 708-717.
[16] Vachaud G. and Thony J.L., 1971. Hysteresis during infiltration and redistribution in a soil column at different initial water contents, *Water Resources Research*, 7(1), 111-127.
[17] Wang Q., Horton R. and Shao M., 2002. Horizontal infiltration method for determining Brooks-Corey model parameters. *Soil Science Society of America*, 66, 1733-1739.
[18] Wang Q., Shao M. and Horton R., 2004. A simple method for estimating water diffusivity of unsaturated soils. *Soil Science Society of America*, 68, 713-718.
[19] Whisler F.O., Klute A. and Peters P.D., 1968. Soil Water Diffusivity from Horizontal Infiltration, *Soil Science Society of America Proceedings*, 32, 6-11

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Flow field experiments in a channel with artificial vegetation

A. Mavrommatis, G. Christodoulou*

Applied Hydraulics Laboratory, School of Civil Engineering, National Technical University of Athens,
5 Heroon Polytechniou, Zografou 15780, Greece
*Corresponding author: Email: christod@hydro.ntua.gr

Abstract

Vegetation is an integral part of river environment, covering a wide range from flexible low grass to bushes or trees with rigid stems. In general, the presence of vegetation affects considerably the flow field, increasing flow resistance, altering local flow conditions and promoting sedimentation of suspended material and light penetration. Therefore the study of flow through vegetation is indispensable for developing river management strategies incorporating flood control, environmental and ecological objectives. The key to this aim is the understanding and quantification of physical processes governing the complex interaction between water flow and vegetation. Despite considerable research on various aspects of flow through vegetation, there is no systematic investigation of the effect of element geometry on the flow field.

Experimental measurements were conducted in a laboratory channel with artificial vegetation simulated by compound elements consisting of a sphere on top of a thin rod for various flow conditions. The elements were placed in three patterns, with densities of 100, 200 and 400 stems/m^2. Velocity profiles and turbulent shear stresses were measured by means of a 3-D ADV instrument at selected locations within the vegetation array. The results indicate a significant decrease of longitudinal velocity in most points, especially at the level of the sphere and between successive elements in the flow direction. Also, large and highly non-uniformly distributed shear stresses are observed. The results suggest that the effect of vegetation elements is higher close to them and at the level of their larger volume, not necessarily near the bed.

Keywords: *open channel flow; vegetation; velocity profiles; shear stress*

1. INTRODUCTION

The presence of vegetation in rivers, streams and riparian zones affects significantly the flow field and consequently the resistance, pollutant dispersion, sediment transport and ecological habitat. Vegetation is an integral part of river environment, covering a wide range of conditions from flexible low grass to bushes or trees with rigid stems. Furthermore, in vegetated areas dissolved nutrients and contaminants tend to accumulate. In general, the presence of vegetation affects considerably the flow field, increasing flow resistance, altering local flow conditions and promoting sedimentation of suspended material. Besides, the low flow environment within vegetated areas provides shelter for fish and aquatic invertebrates. Therefore the study of flow through vegetation is indispensable for developing river management strategies incorporating flood protection, environmental and ecological objectives. The key to this aim is the understanding and quantification of physical processes governing the complex interaction between water flow and vegetation. For this reason, a lot of research has been carried out in recent years on various aspects of flow through vegetation. A comprehensive overview of the hydrodynamic features of such flows is given by Nepf [1]. Much work has focused on the resistance characteristics of the vegetation canopy, initially

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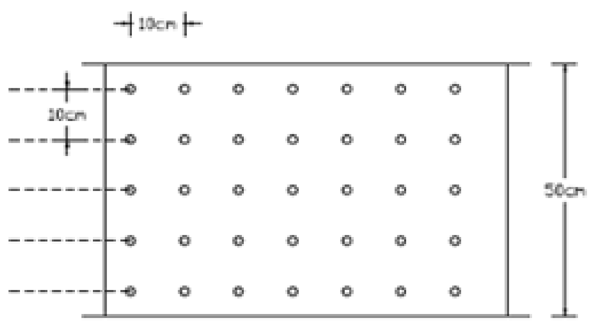
simulated as an array of cylindrical elements, e.g. Stone and Shen [2]. Also, studies on flow field characteristics have been performed, such as by Dunn et al [3] and Fairbanks [4] for rigid elements, Velasco et al [5] and Carollo et al [6] for flexible elements. Numerical simulation of flow and turbulence in vegetated channels has also been attempted, e.g. by López and García [7] and by Souliotis and Prinos [8]. According to Kostidou and Christodoulou [9] the element geometry affects very significantly the overall resistance. However, there is no systematic investigation of the effect of element geometry on the flow field.

The aim of the present paper is to assess the effect of an array of compound rigid elements, resembling submerged small plants, on key features of the flow field, namely the velocity profiles and turbulent stresses. It is part of an on-going study of the flow field for a variety of elements' geometry and density, so as to identify and quantify the most significant parameters affecting the flow. This is considered as a necessary first stage before proceeding to flexible elements, which have the additional complexity of reconfiguration in response to the flow [1].

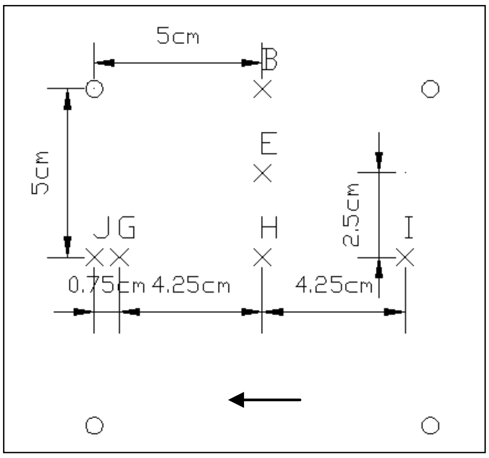
2. EXPERIMENTS

The experiments were conducted in a laboratory flume, 16 m long and 0.50 m wide, with slope 0.001. A perforated bottom was installed, on which the vegetation elements were mounted in the middle part of the flume, 8 m long. The flow depth was controlled by a sluice gate located at the end of the flume to achieve a constant depth over the vegetation area. Each element consisted of a 3 cm diameter plastic sphere attached on top of a rigid rod, 5 cm high and 0.8 cm in diameter. The elements were placed on a 10x10 cm mesh, i.e. with plan density 100 stems/m^2, as shown in Fig. 1(a). Two flow rates were applied and for each of them two flow depths. Baseline runs were also conducted to obtain the flow conditions for the same flow rates and depths with no vegetation for comparison purposes.

The flow discharge was measured by means of a venturi meter and a differential manometer installed in the laboratory supply line, whereas the flow depth was recorded by a point gauge along the flume axis. Velocity measurements were obtained by means of a 3-D ADV instrument (ADV Lab Ver. 2.7 Probe N0187 Nortec AS) on vertical lines at selected locations within the vegetation array and downstream of it.



(a)



(b)

Figure 1. (a) Plan view of vegetation arrangement; (b) location of measurement points presented (arrow denotes the flow direction).

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3. RESULTS AND DISCUSSION

Sample results are shown below, for the case of discharge Q = 22.4 l/s and depth h = 15.4 cm, for six measurement locations within a 10x10 cm cell of the vegetation array, as shown in Fig. 1b, and two locations on the channel axis downstream of the vegetation, at distances 50 and 100 cm. Figures 2, 3 and 4 show the (temporal) mean longitudinal velocity (U_x) profiles and the turbulent stresses ($U'_xU'_z$) along the vertical at these locations. Specifically, Fig. 2 presents the results at locations across the channel (B, E, H), whereas Fig. 3 shows the results at locations along the main flow direction (I, H, G, J). Fig. 4 includes the two locations downstream of the array (T1 at 50 cm, T2 at 100 cm). For comparison, the respective profiles for flow without vegetation are included in the figures.

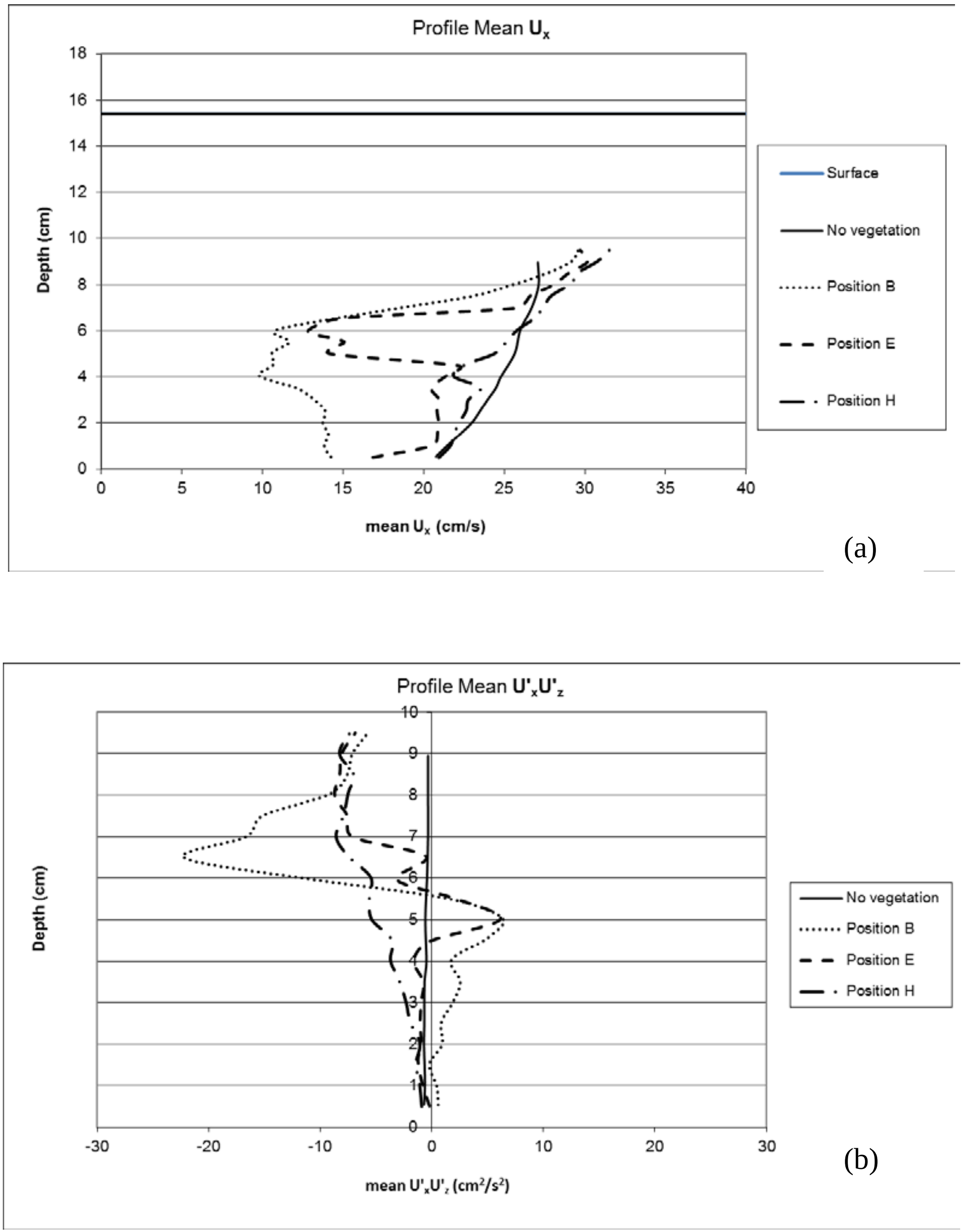
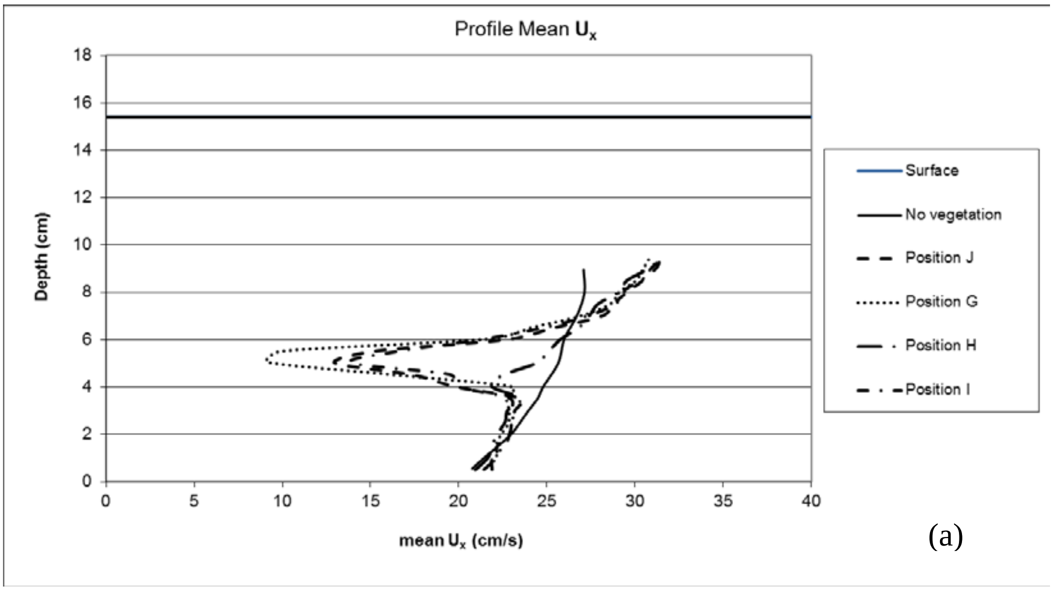


Figure 2. Vertical profiles of mean (a) U_x and (b) $U'_xU'_z$ at locations across the main flow within the vegetation

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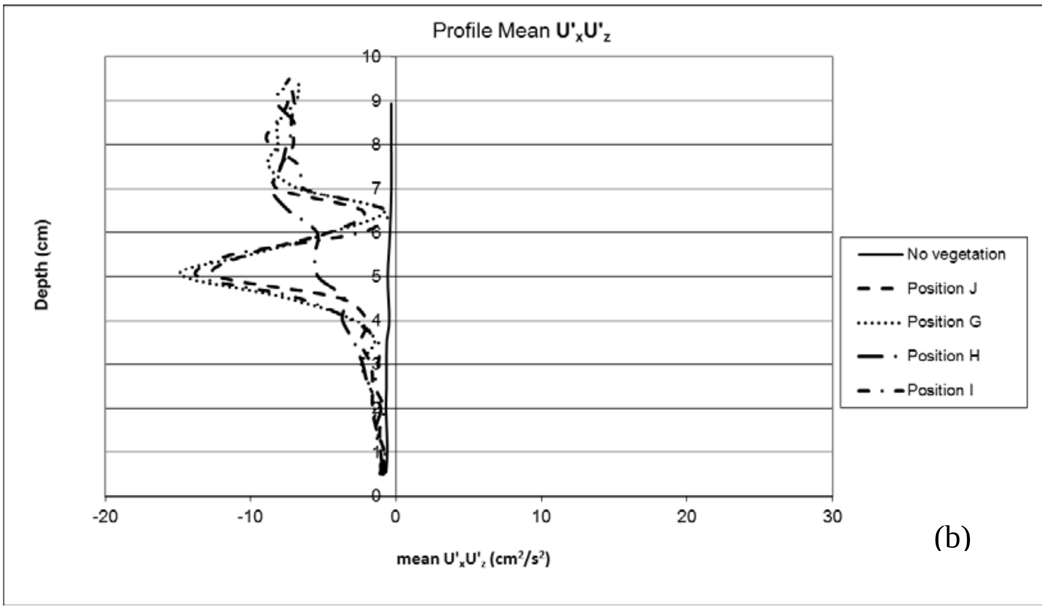


Figure 3. Vertical profiles of mean (a) U_x and (b) $U'_xU'_z$ at locations along the main flow within the vegetation

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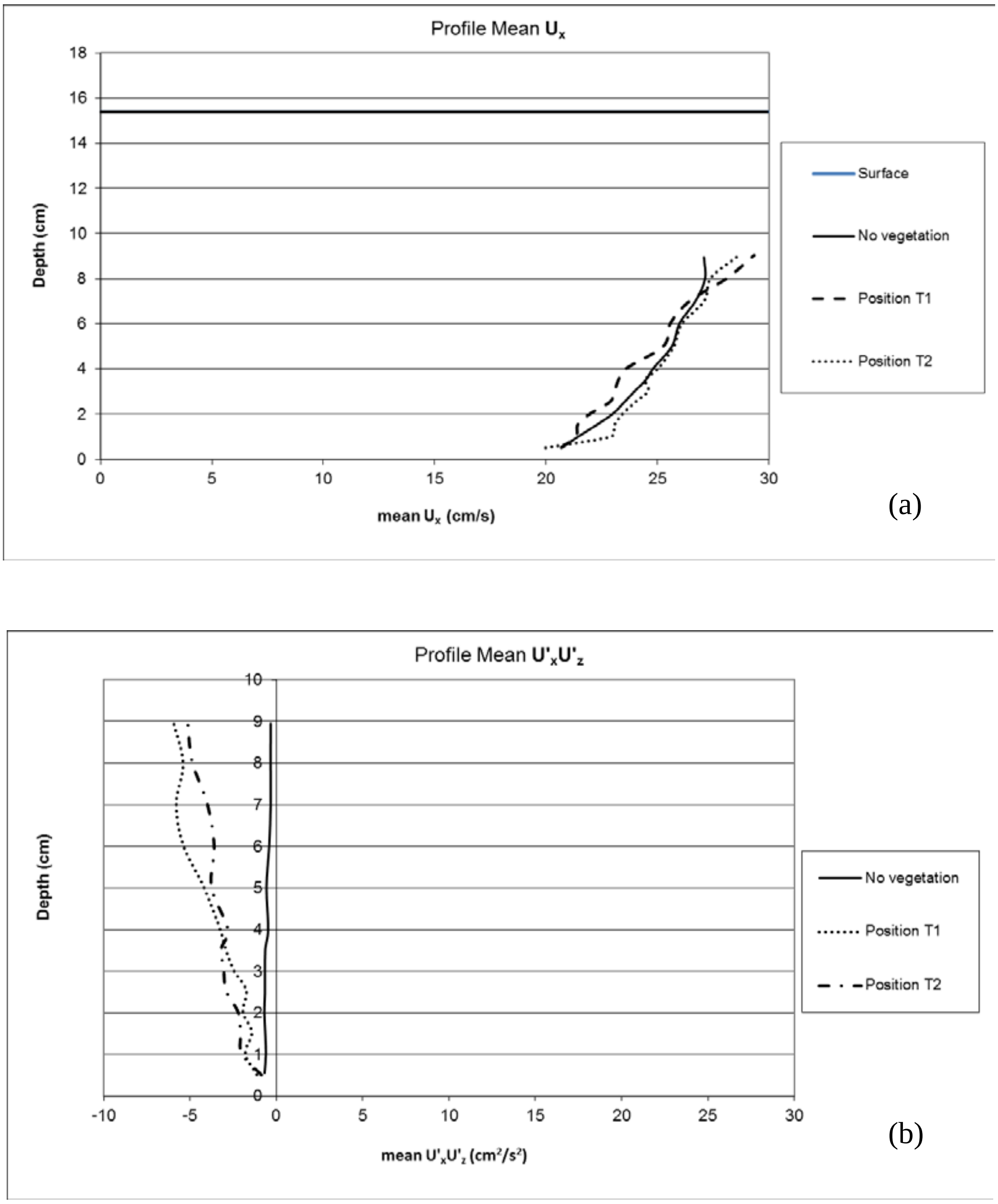


Figure 4. Vertical profiles of mean (a) U_x and (b) $U'_xU'_z$ on the channel axis downstream of the vegetation

A very pronounced velocity defect is observed in most locations within the vegetation. In particular, as we move across the channel the maximum effect of vegetation is seen at point B, i.e. at the mid-point between elements in the flow direction, where the velocity defect extends well below the spherical part of the element. A significant velocity defect is also observed at point E, but more restricted vertically, roughly at the level of the sphere. The least deviation from the no-vegetation velocity profile occurs at point H (center of the 10x10 cell). Concerning the longitudinal section at the mid-distance between elements, nearly the same velocity profile is observed at most points (G, J, I), with sharp decrease of velocity at the level of the bottom of the sphere. It is noticeable that in all cases the observed velocity defect within the vegetation mimic array seems to be compensated in the region above the elements. Concerning the downstream points T1 and T2, the effect of the vegetated area on the velocity profile is minor and diminishing with distance.

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Regarding the xz turbulent stresses, much higher values compared to the no-vegetation case are observed, generally increasing upwards. Of particular notice is the highly non-uniform distribution occurring at most measurement locations within the vegetation array, indicating the development of intense shear layers. It is also noticed that high turbulent stresses persist downstream of the vegetated area, despite the fact that the main velocity has almost returned to the no-vegetation profile.

4. CONCLUSIONS

Indicative results are presented of an on-going experimental study aiming at the assessment of the effect of geometry of vegetation elements on the flow characteristics. They concern the velocity and shear stress profiles within an array of compound rigid vegetation elements consisting of a sphere on top of a rod, placed with plan density of 100 stems/m^2. Very significant reduction of longitudinal velocity in most points within the vegetation array, especially at the level of the sphere and between successive elements in the flow direction, was observed as well as large and highly non-uniformly distributed shear stresses. The results suggest that the effect of vegetation elements is higher close to them and at the level of their larger volume, not necessarily near the bed. Further work proceeds with more measurement points, flow conditions, density and geometry of elements.

References

[1] Nepf, H.M., 2012. Hydrodynamics of vegetated channels. *Journal of Hydraulic Research*, **50 (3)**, 262-279.

[2] Stone, B.M., Shen, H.T., 2002. Hydraulic resistance of flow in channels with cylindrical roughness. *Journal of Hydraulic Engineering*, **128 (5)**, 500-506.

[3] Dunn, C., Lopez, F., Garcia, M.H., 1996. Mean flow and turbulence in a laboratory channel with simulated vegetation. *Hydraulic Eng. Ser.51*, University of Illinois, Urbana, IL.

[4] Fairbanks, J. D., 1998. Velocity and turbulence characteristics in flows through rigid vegetation", MS Thesis, Virginia Polytechnic Institute & State University, Blacksburg, VA, USA.

[5] Velasco, D., Bateman, A., Redondo, J.M., Demedina, V., 2003. An open channel flow experimental and theoretical study of resistance and turbulent characterization over flexible vegetated linings. *Flow, Turbulence and Combustion*, **70**, 69–88.

[6] Carollo, F.G., Ferro, V., Termini, D., 2002. Flow velocity measurements in vegetated channels. *Journal of Hydraulic Engineering*, **128 (7)**, 664-673.

[7] López, F., García, M., 2001. Mean Flow and Turbulence Structure of Open-Channel Flow through Non-Emergent Vegetation. *Journal of Hydraulic Engineering* (ASCE), **127 (5)**, 392-402.

[8] Souliotis, D., Prinos, P., 2008. Turbulence in vegetated flows: Volume-average analysis and modelling aspects. *Acta Geophysica*, **56 (3)**, 894-917.

[9] Kostidou, E.P., Christodoulou, G.C., 2015. Equivalent roughness of artificial vegetation in subcritical flow. *E-Proc. of the 36th IAHR World Congress*, The Hague, Netherlands.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
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Groundwater management optimization with combined use of Harmony Search Algorithm and modular finite-difference flow model Modflow

M. Antoniou, N. Theodossiou*, D. Karakatsanis

Division of Hydraulics and Environmental Engineering, Department of Civil Engineering,
Aristotle University of Thessaloniki, Thessaloniki, Greece
*Corresponding author: Email: niktheod@civil.auth.gr

Abstract

This study examines a groundwater management model, in which the solution is obtained through a combined simulation- optimization model. The most widely used numerical groundwater flow model, MODFLOW, which is a three-dimensional model that uses finite difference method for solving the governing groundwater flow equation, is used as the simulation model. This model is then connected to the harmony search algorithm, one of the most emerging and successful meta-heuristic optimization techniques, which simulates the quest for perfect harmony in music. In this paper, this technique is applied to a theoretical example found in the manual of Modflow for comparison purposes, by examining the optimization of its aquifer system in terms of minimizing the cost of pumping drilling. For this application a specially designed computer software programmed in MATLAB environment is developed, while the created software allows users to have a visual image of the piezometric surface in the whole aquifer system area through plotted graphs. More specifically, while the positions of the pumping wells and the total required demand for the pumping wells from the three aquifers system are known in advance, the optimal spatial distribution of the pumping rates is determined. The results show that the combined model provides a very useful solution and can be used to solve complex groundwater management problems.

Keywords: groundwater resource management; groundwater flow simulation model; Modflow; Harmony search algorithm; optimization

1. INTRODUCTION

Since groundwater aquifers constitute one of the main sources of water for domestic and agricultural use, intense measures for ensuring good quality and sufficient quantity, are demanded. For this reason, it is of most importance to develop suitable simulation and optimization models for the determination of the optimal operation of pumping wells, in order to ensure the maximum coverage of the demands while at the same time, keeping the operational and maintenance cost of the system to a minimum and respecting the protection of the environment.

Groundwater mathematical flow-simulation models, considered to be absolutely necessary tools for the rational management, are usually non-linear [1]. These models are often combined with optimization algorithms in order to determine the optimal policy amongst a number of potential alternatives. A novel metaheuristic optimization algorithm, the Harmony Search Algorithm (HSA) was introduced in 2001 by Geem et al. [2].

Ayvez [3] applied the HS algorithm combined with the use of the groundwater flow-simulation model MODFLOW and concluded that this algorithm can successfully converge to at least the

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same, and in some cases better, solutions than those derived from the application of other methods attempting to solve the same problem.

The main target of this paper in the development of a groundwater management tool that can combine the tree-dimensional flow-simulation model MODFLOW with the Harmony Search Algorithm. For this reason, a theoretical problem with a known solution, in order to test the results, was used. The software combining the simulation and the optimization models was developed under the Matlab environment.

2. HARMONY SEARCH ALGORITHM

The Harmony Search Algorithm (HSA) is a metaheuristic optimization method inspired by music harmony. It was first introduced by Zong Woo Geem in his PhD thesis [4]. This algorithm is based on a stochastic random search technique whose natural corresponding system is the process for the search of a better harmony by musicians. The simplicity, the easy of convergence and the simple programming of the algorithm have contributed in the spreading of the applications of HSA in various fields. HSA applies the three following procedures in every iteration. Procedure ‘b’ is used (in a percentage) only if procedure ‘a’ is activated. Option ‘c’ is applied every time procedure ‘a’ is not selected:

a. HS is choosing any value from HS Memory. This process is defined as Memory Consideration and it is very important because it ensures that good harmonies (values that give good results) will be considered through the solution. Moreover, these “good” harmonies will be the material (similar with parents in GA) for the creation of new, even better harmonies. In order to use this process effectively, Harmony Memory Considering Rate (HMCR) was defined. This index will specify the probability that new harmony will include a value from the historic values that are stored in the Harmony Memory. If this rate is too low, only few elite harmonies will be selected. As a result HSA will converge slowly. Of course an HMCR value of 1.0 is not recommended because the exploration of the entire feasible range will be obstructed and optimization will fail. Typical values of HMCR are always greater than 70%.
b. Every component of the new harmony chosen from HM, is likely to be pitch-adjusted. For example a Pitch Adjusting Rate (PAR) of 10%, indicates that algorithm will choose neighboring values for the 10% of the harmonies chosen from HM. The new harmony will include the value x_i^{new} which will be:

    $x_i^{new} = x_i \pm Random \cdot bw$,

    where, x_i is the existing pitch stored in HM,
    Random is a random number between 0 and 1, and
    bw is the bandwidth of the adjustment
c. The third choice is to select a totally random value from the possible value range. Randomization occurs with probability (100-HMCR)% and increases the diversity of the solutions. Although pitch adjustment has a similar role, it is limited in a local area. Randomization can drive the algorithm to explore the whole range and attain the global optimality.

3. MODFLOW

MODFLOW (Modular three dimensional finite difference ground water flow model) developed by U.S.G.S. is one of the most widely used groundwater flow-simulation models. MODFLOW is an open source program written in FORTRAN using a deterministic finite differences numerical scheme.

The governing three-dimensional flow equation used by MODFLOW [5, 6] combines the Darcy law with the conservation of mass principle through the following equation:

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$$Ss\frac{\partial h}{\partial t}=\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)-W \tag{3.1}$$

where:
K_{xx}, K_{yy}, K_{zz}: are the values of the hydraulic conductivity along the three axes x, y and z (L/T) considered to be parallel to the main directions of flow, h, the hydraulic head (L), W, represents the sources and sinks (T^{-1}), S_s, is the storativity coefficient (L^{-1}) and t, the time (T).

4. DESCRIPTION OF THE APPLICATION

The application used in order to demonstrate the proposed methodology was introduced by Michael G. McDonald and Arlen W. Harbaugh in 1988 [6] during the presentation of MODFLOW and it is still considered to be a prototype for the formulation of the input and output files of the software. This is why the problem is relatively simple but at the same time comprises several complex elements in order to demonstrate to the users the multi-dimensional possibilities of MODFLOW and the way they are introduced in the formulation of the input and output files and the processes for the discretization of the grid.

This application comprises three permeable layers separated from each other by impermeable layers. The boundary conditions include a constant head boundary to the east simulating an existing lake. The aquifer system is replenished by infiltrating precipitation which is added to the first permeable layer. Outflows are a result of underground drains distributed across the first layer in different depths, of 15 pumping wells and of the proximity to the lake. Figure 1, presents the characteristics of the aquifer system. All layers are considered to be horizontal. The flow is steady-state, the aquifer is considered homogeneous and isotropic. Figure 2 presents the exact positions of the drains and the pumping wells. According to the reference status, the quantity of water pumped from each pumping well is considered to be 5 ft^3/s.

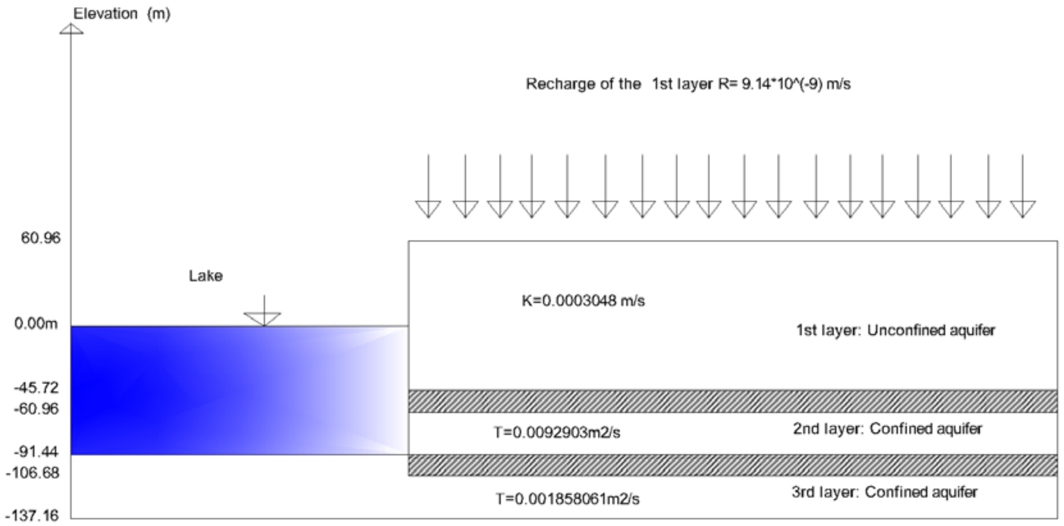


Figure 1 Side-view of the aquifer system

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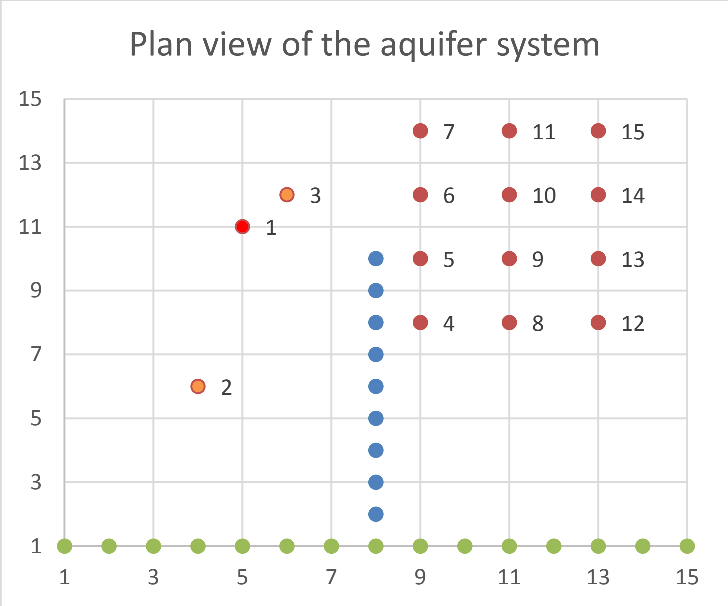


Figure 2 Plan-view of the aquifer system. Active wells pumping from the 1st layer are represented in orange, those from the 2nd layer, in green and those from the 3rd layer, in red. Blue dots represent the drains while grey ones, the constant head boundary.

The optimization problem incorporated within the management model calls for the optimal re-distribution of the amount of water pumped from each one of these 15 pumping wells. The number of wells and their position are considered to be known and constant. The decision variables of the optimization model are the determination of the pumping rate of each well considering that they lie within pre-defined boundaries. The objective function of the optimization model is defined as the pumping cost expressed as the product of the pumping rate and the water-level drop at each well location (equation 1).

$$z = min\left\{\sum_{i=1}^{N} s_i * Q_i\right\} \tag{1}$$

The constrains of the optimization model are:

- The total amount of water abstracted from these wells must be at least equal to the total demand, as expressed by the current practices.

$$\sum_{i=1}^{N} Q_i \geq \tilde{Q} \tag{2}$$

where $\tilde{Q}$ =75 ft^3/s.

- The pumping rate of each well must lie within a pre-defined range in order to avoid dewatering of the aquifer.

$$Q_{min} \leq Q_i \leq Q_{max} \tag{3}$$
$$0 \leq Q_i \leq 10 \text{ ft}^3/\text{s} \tag{4}$$

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5. COMBINED USE OF SIMULATION AND OPTIMIZATION MODELS

A special software was developed using the MATLAB environment aiming at the combined use of the flow-simulation model (MODFLOW) and the optimization technique (HS algorithm). In the flow chart presented in figure 3, the proposed methodology is graphically demonstrated through the structure of the developed software. More specifically, during the 2nd step, after the creation of the harmony memory HM, the resulting pumping rates Q_i are corresponded to the actual wells i. The input files for MODFLOW are then created through this special software and then the simulation model is executed. The hydraulic heads are then calculated at the positions of the wells and the differences to the initial ones (for each one of the aquifers) are recorded as the water-level drop. The pumping cost as expressed by equation 1, defines the objective function of the optimization model. The special software also formulates the constrains and then executes the optimization algorithm. The results of the optimization model are then re-directed, if necessary to the simulation model etc. The whole procedure ends when no further optimization can be achieved.

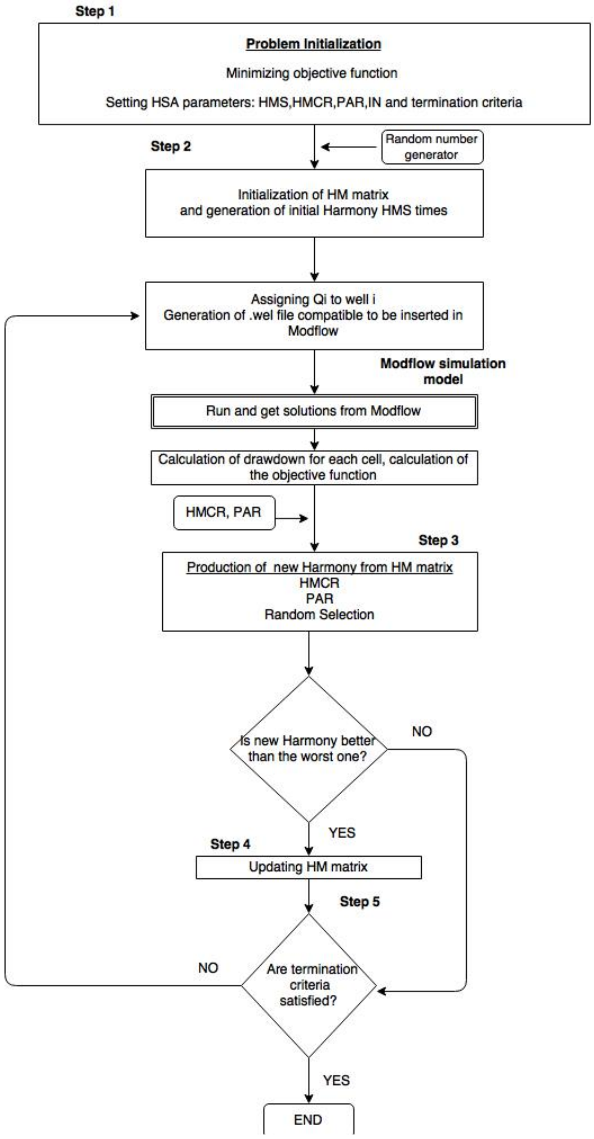


Figure 3 Flow chart of the proposed methodology as described by the special software developed to combine the use of the simulation and optimization models

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6. RESULTS OF NUMERICAL APPLICATION

The program was executed for various combinations of the optimization model parameters. The best solution was accomplished using the combination HMS=50, HMCR=0.7, PAR=0.5 and IN=41797. This solution results to a pumping cost and a total water-level drop 18% and 14% lower than that corresponding to the reference status. The developed combining software has been programmed so that it can also produce graphical representations of the water-level distribution in the form of 3-D graphs (figures 4 and 5) as well as 2-D contours (figure 7). This representation is also available not only for the top layer, but for the underlying layers as well (figure 6).

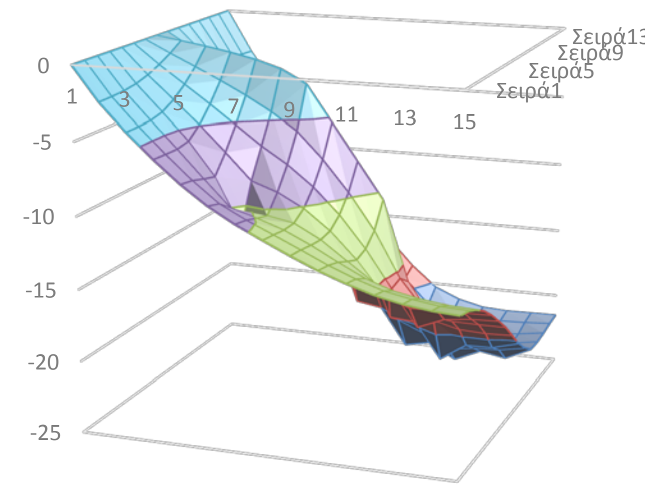


Figure 4 3-D representation of water-level drop for the top aquifer under operating pumping wells conditions (m)

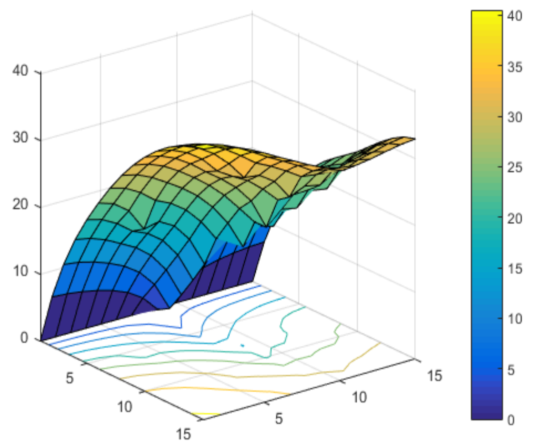


Figure 5 3-D representation of the hydraulic head distribution for the top layer under operating pumping wells conditions (m)

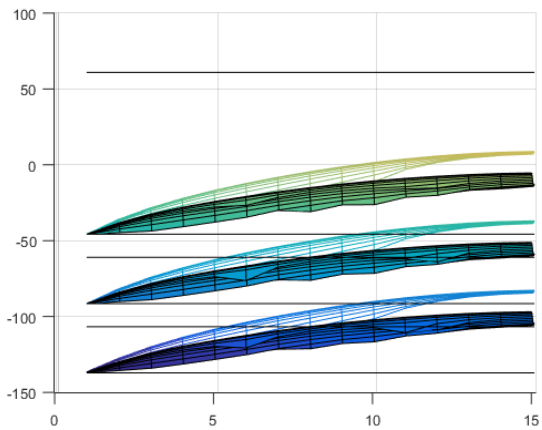


Figure 6 Side view of the hydraulic head distribution before the operation of the wells (transparent grid) and during the operation of the wells (colored grid)

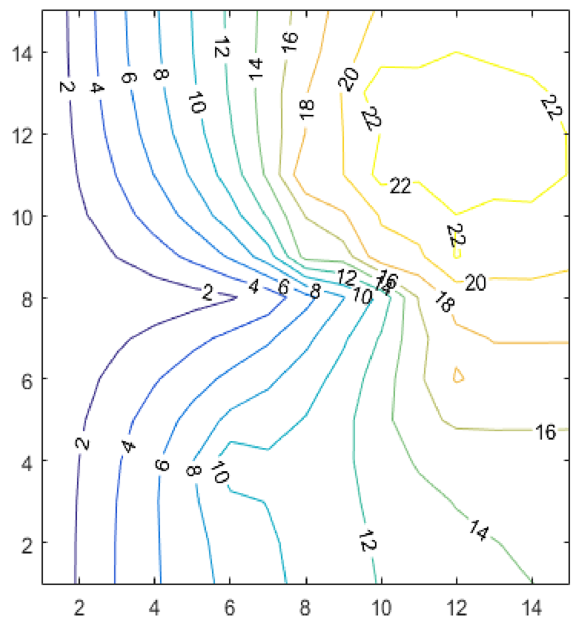


Figure 7 Contours demonstrating equal water-level drop for the top aquifer under operating pumping wells conditions

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7. CONCLUSION

In this paper, a methodology is presented for the combined use of a flow-simulation model with an optimization algorithm aiming at the rational and optimal management of groundwater aquifer systems. One of the most widely used and most efficient three-dimensional flow-simulation models, MODFLOW is used combined with the Harmony Search Algorithm, one of the novel metaheuristic optimization techniques. These two models are combined with a specially designed software developed under the MATLAB environment, formulating a powerful, user friendly and effective management tool.

In order to investigate the efficiency of the developed combining software and the proposed methodology, a classic example of the application of MODFLOW was used. This example was optimized using the operational cost as the objective function. A logical number of iterations was needed for the achievement of the optimal solution encouraging the use of the proposed methodology in similar problems.

The results of the presented methodology demonstrate that the combined use of a groundwater flow-simulation model like MODFLOW with an efficient optimization technique like HS algorithm can formulate a very effective management tool. The graphical representation of the outputs, as provided by the developed software, offers the user a visualization of the results of alternative solutions, thus assisting the understanding of the impacts of the application of complex management policies.

REFERENCES

[1] Theodossiou, N., 2000. Optimization techniques in groundwater resources management, Department of Civil Engineering Aristotle University of Thessaloniki (in Greek).

[2] Geem Z.W., J.-H. Kim, G.V. Loganathan, 2001. *A new heuristic optimization algorithm: harmony search Simulation*, 76 (2), pp. 60–68

[3] Ayvaz M. T., 2009. *Application of harmony search algorithm to the solution of groundwater management models*, Advances in Water Resources, Vol. 32, pp. 916-924

[4] Geem, Z., 2000. *Optimal design of water distribution networks using harmony search*, PhD thesis, Korea University

[5] McDonald, M.G., and A.W. Harbaugh, 1988. *A modular three-dimensional finite-difference ground-water flow model*, U.S. Geological Survey Techniques of Water-Resources Investigations, Book 6, Chapter A1.

[6] Harbaugh, A.W., E.R. Banta, M.C. Hill, M.G. McDonald, 2000. *MODFLOW-2000, the U.S. Geological Survey modular ground-water model - User guide to modularization concepts and the ground-water flow process*, U.S. Geological Survey Open-File Report 00-92.

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Crop coefficient estimation for the cultivations in North West Greece

G. Arampatzis[1*], C. Evangelides[2], M. Nikou[2]

[1]Soil and Water Resources Institute, Hellenic Agricultural Organisation-DEMETER, 57400 Sindos, Greece.
[2]Department of Hydraulics and Transportation Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
*Corresponding author: Email: arampgeo@gmail.com

Abstract

Crop evapotranspiration is usually estimated using predictive models. Most of them require several meteorological data as in Penman-Monteith method by FAO 54, which is accepted as the most accurate method. Most of times though, there is not sufficient data for all the parameters required by the above method. In these cases, the necessity of calculating the crops water requirements, leads to less data demanding evapotranspiration methods. The calculation of actual crop water requirements requires the knowledge of reference evapotranspiration and also the crop coefficient. The aim of this paper is to estimate the crop coefficients of the typical cultivations (beet, maize, beans, potatoes, peppers, wheat and barley) in North West Greece. In this area the crop coefficients have been determined only for the Penman-Monteith method. These coefficients were used as a base in order to extract coefficients for Hargreaves method and Blaney-Criddle by FAO 24. Meteorological data from the meteorological station of the municipality of Amyntaio in North West Greece was utilized for the calculation of reference evapotransiration with three methods. Knowledge for the Penman Monteith reference evapotranspiration and the corresponding crop coefficients led to calculation of the crop evapotranspiration. Based on these results, crop coefficients were estimated for the other two methods.

Keywords: crop coefficient; crop evapotranspiration; meteorological data

1. INTRODUCTION

The water requirements of crops depends on the type of crop and the pace of their requirements, quantitative and temporal, determines the size of the vegetation which does not necessarily correspond to the optimization of production. But to maximize the economic result and the needs of a growing water should always be consistent with environmental protection.

The calculation of reference evapotranspiration (ET_O) of crops is a prerequisite for the rational irrigation scheduling and optimization of agricultural production. Most of the modern methods, that are utilized to calculate the evapotranspiration of a specific crop, include two steps. The first step is the evapotranspiration estimation of a well irrigated reference crop which is called reference evapotranspiration and is denoted as ETo. The reference crop is a grass reference crop with specific characteristics. The second step consists of the calculation of the crop evapotranspiration of the cultivation which is denoted as ETc. The ETc is obtained by multiplying ETo with a "crop coefficient" (kc), which is specific for each cultivation and for each ETo method (Doorenbos & Pruitt, 1977; Jensen et al., 1990; Allen et al., 1998; Papazafiriou, 1999; Panoras et al., 2001). The crop coefficient is not constant, but varies during the growing stage of the cultivation. From the available methods for the calculation of the reference evapotranspiration, the ones using a plurality of meteorological data, are considered to be the most accurate ones as Penman (1956), Doorenbos & Pruitt (1977), Jensen et al. (1990), Allen et al. (1998). The Penman-Monteith method by FAO 56

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(Allen et al., 1998) has been proven as the most popular and accurate method for a number of regions. Additionally, the calculated values of the method are considered particularly accurate for the areas in Greece (Sakellariou-Makrantonaki et al., 1996; Georgiou et al, 2000; Alexiou et al, 2000).

Even though the Penman-Monteith method by FAO 56 is the most accurate one it cannot be utilized often due to lack of required meteorological data. This fact forces researchers to use methods requiring fewer meteorological data such as Hargreaves (Hargreaves et al., 1985) and Blaney-Criddle by FAO 24 (Doorenbos & Pruitt, 1977).

Values of the crop coefficient for each cultivation are established for the four stages of crop growth: a) the initial establishment, b) crop development, c) effective full cover to the start of maturity and d) start of maturity to harvest. During the initial establishment stage, where water loss occurs mostly due to the evaporation of water from the surface, the value of the crop coefficient (K_{cini}) is steady. During the crop development stage a linear increase in the value of the crop coefficient occurs in order to reach and remain at the highest level for the effective full cover to the start of maturity stage (K_{cmid}). At the final stage of the cycle a linear reduction in the value of the crop coefficient occurs from (K_{cmid}) to the end point (K_{cend}).

The aim of this paper is to estimate the crop coefficients of the typical cultivations (beet, maize, beans, potatoes, peppers, wheat and barley) in North West Greece. In this area the crop coefficients have been determined only for the Penman-Monteith method (Allen et al., 1998). These coefficients were used as a base in order to extract coefficients for Hargreaves method (Hargreaves et al., 1985) and Blaney-Criddle by FAO 24 (Doorenbos & Pruitt, 1977). Meteorological data from the meteorological station of the municipality of Amyntaio in North West Greece was utilized for the calculation of reference evapotranspiration with three methods. Knowledge for the Penman Monteith reference evapotranspiration and the corresponding crop coefficients led to calculation of the crop evapotranspiration. Based on these results, crop coefficients were estimated for the other two methods.

2. THEORY

The net claims of crop water calculated from the relationship:

$$I_n = ET_c - (P_e + G_w + SM) \quad (1)$$

where: I_n is the net water requirements, P_e is the monthly beneficial rain (Papazafiriou, 1999), G_w is the contribution of underground horizon, SM is the water stored in the root zone area at the beginning of the growing season and can be used from crops.

The crop evapotranspiration is expressed:

$$ET_C = k_C \, ET_o \quad (2)$$

where: ETo is the reference evapotranspiration, ETc is the crop evapotranspiration, kc the crop coefficient.

Using the Penman-Monteith method by FAO 56 (Allen et al., 1998) the ET_o is calculated by the relationship:

$$ET_o = \left[0.408\Delta\,(R_n - G) + \gamma \frac{900}{T+273} u_2\left(e_s - e_a\right)\right] [\Delta + \gamma(1 + 0{,}34u_2)]^{-1} \quad (3)$$

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where: ETo is the reference evapotranspiration in mm / day, Rn is total net radiation at the crop surface in MJ $m^{-2}day^{-1}$, G is the daily soil heat flux density in MJ $m^{-2}day^{-1}$, γ is the psychrometric constant kPa^oC^{-1}, e_s is the saturation vapour pressure in kPa, ea is the actual vapor pressure in kPa, T is the mean daily temperature of air at 2 m above the earth's surface in ^oC and is given by:

$$T = \frac{T_{max}+T_{min}}{2} \tag{4}$$

u_2 is the wind speed at 2 m above the earth's surface in m / sec and is given by:

$$u_2 = \frac{4{,}87u_z}{\ln(67{,}8z-5{,}42)}. \tag{5}$$

where uz speed of wind at z m above the earth's surface, e_s is the pressure of saturated water vapor in kPa, e_a is the actual vapor pressure in kPa, Δ is the slope of the vapor pressure curve in kPa^oC^{-1} and is given by:

$$\Delta = 4098\frac{\left[0{,}6108e\left(\frac{17{,}27T}{T+237{,}3}\right)\right]}{(T+237{,}3)^2} \tag{6}$$

Using the Hargreaves method (1985), which is often selected, because of limited availability of meteorological data, ET_0 is expressed as:

$$ET_o = 0{,}0023R_a(T_{mean} + 17{,}8)(T_{max} - T_{min})^{0{,}5}. \tag{7}$$

wherein ET_o reference evapotranspiration in mm • day^{-1}, T_{mean}, T_{max}, T_{min}, the average, maximum and minimum air temperature at a height of 2m at ^oC respectively, Ra extraterrestrial radiation in mm/d. This method is considered reliable enough (Hargreaves and Allen, 2003).

The method Blaney Criddle at FAO 24 (Doorenbos & Pruitt, 1977) for calculating ETo using the relationship:

$$ET_o = a + bf \tag{8}$$

wherein ETo is the reference evapotranspiration in mm d^{-1} , a factor is given by the relation

$$a = 0{,}0043RH_{min} - \frac{n}{N} - 1,$$

wherein RHmin is the minimum relative humidity as a percentage %, n/N is relative sunshine (n is the real sunshine hours, N is the theoretical sunshine hours), b is a coefficient given by tables as a function of the minimum humidity of relative sunshine and wind speed during the day, f is factor of Blaney−Criddle defined by the relationship $f = (0{,}46T + 8{,}13)p$ where T is the mean monthly ambient temperature in °C, and p is the average daytime hours of the year and is given by table.

3. RESULTS AND DISCUSSION

The study area was Amyntaio in NW Greece, where the main crops are sugar beet, maize, beans, potatoes, peppers, wheat and barley. The data utilized was taken from a meteorological station located in the study area. The collected data on daily basis was rain, sunshine, temperature, humidity, solar radiation and wind speed for the period 2008 to 2013. Daily reference evapotranspiration was calculated using the Penman-Monteith method by FAO 56, the Hargreaves method and the Blaney Criddle method by FAO 24.

Crop coefficients for Penman-Monteith method were taken from literature (Abas, 2010). Thus, the daily crop evapotranspiration for the period 2008 to 2013 and for all crops under investigation was calculated. Then, according to Equation 2, the crop coefficients for Hargreaves and Blaney Criddle methods were calculated since the daily crop evapotranspiration was known from the Penman-Monteith method. The effectiveness of this procedure was verified using the correlation coefficient between daily calculated kc values for every year and final kc obtained for each crop and method.

Table 1. Crop coefficients (Abas, 2010) for Penman-Monteith method by FAO 56, growing, sowing and harvest periods for each crop.

	Plant Coefficient			**Growing Season (days)**				**Sowing period**	**Harvest period**
	$K_c$ini	**$K_c$mid**	**$K_c$end**	**1st**	**2nd**	**3rd**	**4th**		
Beet	0.35	1.20	0.60	30	45	90	15	1/03-30/04	When they reach maximum content of sugar
Maize	0.3	1.15	0.35	25	40	60	25	20/04-10/05	5/09-15/09
Beans	0.4	1.15	0.35	15	25	50	20	May	August-November
Potato	0.4	1.15	0.75	30	35	50	25	15/04-25/04	25/08-25/09
Pepper	0.4	1.05	0.90	25	35	35	20	1/05-31/05	July-September
Wheat	0.3	1.15	0.25	20	140	50	20	15/10-30/11	1/7-20/7
Barley	0.3	1.15	0.25	20	130	45	20	15/10-30/11	10/6-10/7

Table 2. Crop coefficients for Hargreaves method, growing, sowing and harvest periods for each crop.

	Crop Coefficient			**Growing Season (days)**				**Sowing period**	**Harvest period**	**Correlation coefficient**
	$K_c$ini	**$K_c$mid**	**$K_c$end**	**1st**	**2nd**	**3rd**	**4th**			
Beet	0.41	1.35	0.61	30	45	90	15	1/03-30/04	When they reach maximum content of sugar	0.91
Maize	0.38	1.33	0.34	25	40	60	25	20/04-10/05	5/09-15/09	0.93
Beans	0.44	1.37	0.37	15	25	50	20	May	August - November	0.89
Potato	0.43	1.38	0.71	30	35	50	25	15/04 - 25/04	25/08-25/09	0.91
Pepper	0.44	1.24	0.83	25	35	35	20	1/05-31/05	July-September	0.92
Wheat	0.21	1.26	0.25	20	140	50	20	15/10-30/11	1/7-20/7	0.87
Barley	0.23	1.27	0.40	20	130	45	20	15/10-30/11	10/6-10/7	0.85

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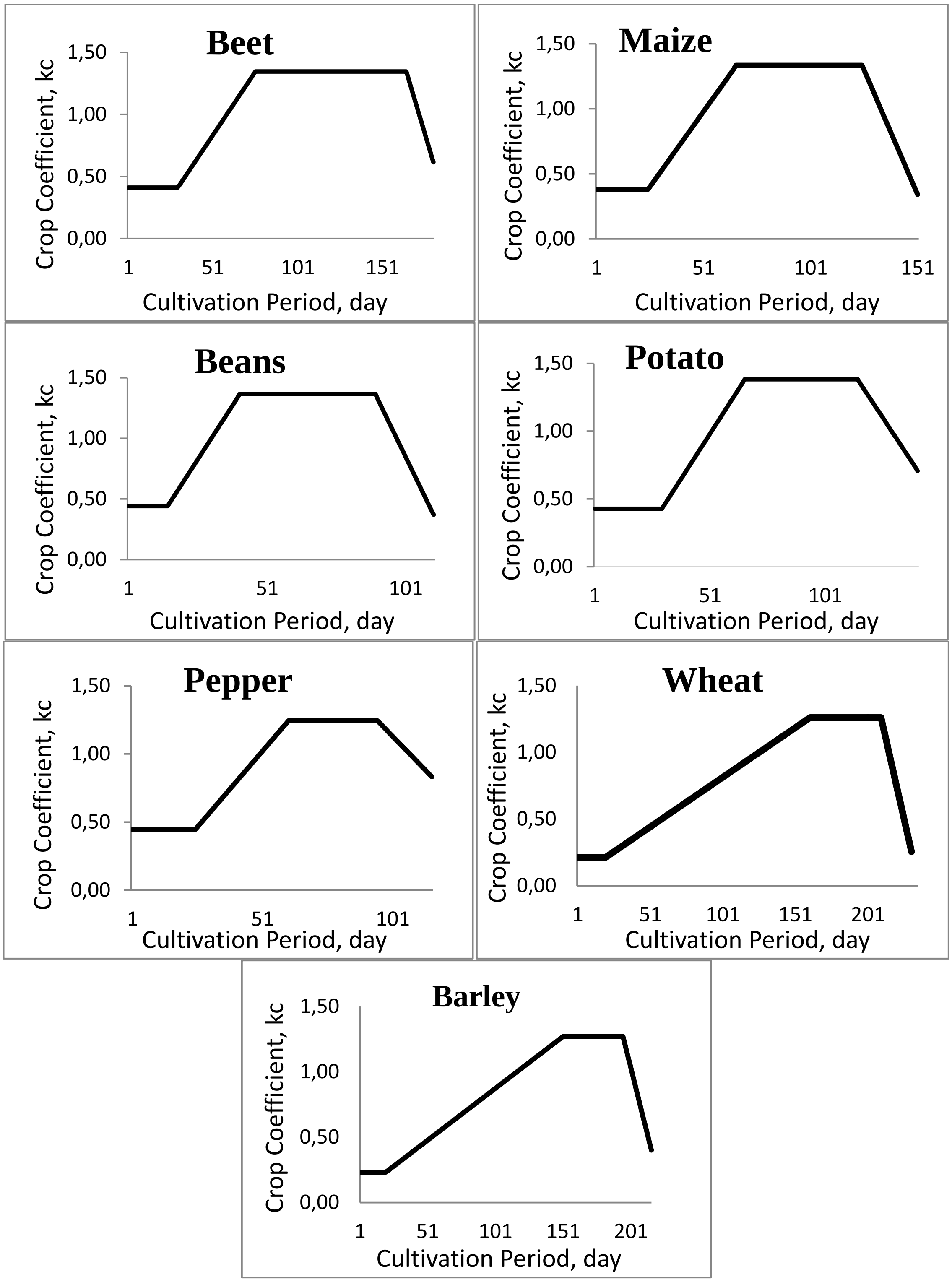


Figure 1. Crop coefficient for Hargreaves et al. (1985)

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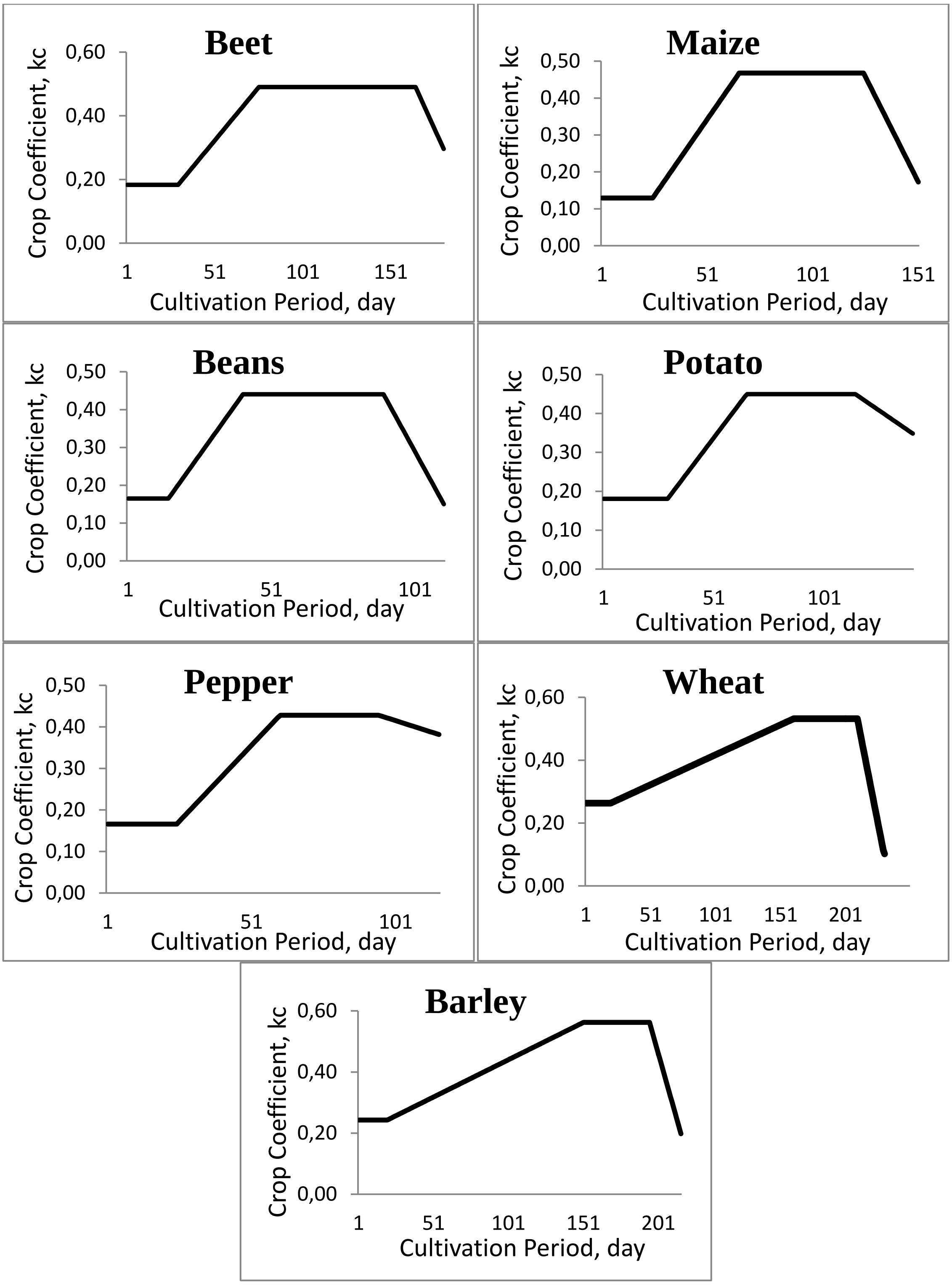


Figure 2. Crop coefficient for Blaney Criddle FAO 24 method.

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Table 3. Crop coefficients for Blaney-Criddle method, growing, sowing and harvest periods for each crop.

	Crop Coefficient			Growing Season (days)				Sowing period	Harvest period	Correlation coefficient
	$K_c$ini	$K_c$mid	$K_c$end	1st	2nd	3rd	4th			
Beet	0.18	0.49	0.30	30	45	90	15	1/03-30/04	When they reach maximum content of sugar	0.91
Maize	0.13	0.47	0.17	25	40	60	25	20/04-10/05	5/09-15/09	0.94
Beans	0.16	0.44	0.15	15	25	50	20	May	August -November	0.91
Potato	0.18	0.45	0.35	30	35	50	25	15/04 -25/04	25/08-25/09	0.92
Pepper	0.17	0.43	0.38	25	35	35	20	1/05-31/05	July-September	0.94
Wheat	0.26	0.53	0.10	20	140	50	20	15/10-30/11	1/7-20/7	0.91
Barley	0.24	0.56	0.20	20	130	45	20	15/10-30/11	10/6-10/7	0.89

4. CONCLUSION

Knowledge of net crop requirements which are necessary for the rational water management requires the estimation of crop evapotranspiration, effective precipitation, soil moisture and the contribution of groundwater. Crop evapotranspiration is calculated from reference evapotranspiration and crop coefficient. In this paper crop coefficients for the main cultivations in NW Greece are established for the Hargreaves and Blaney-Criddle methods as shown in Tables 2 and 3. The same tables contain calculation of a correlation coefficient between daily calculated kc values for every year and final kc obtained for each crop and method.

From the three methods that are used in this paper, the Penman-Monteith method needs the most data and in contrast the Hargreaves method needs the least. The used methodology is quite simple and the crop coefficients that were obtained can be utilized for evapotranspiration methods that do not require many meteorological data.

REFERENCES

[1] Abas V., 2010. Investigation and estimation of meteorological parameters having direct impact in agriculture. Ph.D. Thesis, A.U.Th., pp. 327.

[2] Alexiou I, Kotsopoulos S., Kalfountzos D. and Virlas P., 2000. Estimates of evapotranspiration through soil moisture availability functions. Proceedings of 8th Hellenic Hydrotechnical Association Conference, April 19-21, Athens, 493 – 500.

[3] Allen, R., Pereira, L., Raes, D. and Smith, M., 1998. Crop evapotranspiration. Guidelines for computing crop water requirements. FAO Irrigation and Drainage Paper 56, FAO, Rome, 300 pp.

[4] Georgiou P., Papamichail D. and Papazafiriou Z., 2000. Comparative evaluation of Penman and Penman-Monteith methods using reference evapotranspiration estimation in Greece. Proceedings of 5th Conference on Meteorology – Climatology – Atmospheric Physics, Thessaloniki, 395-402.

[5] Doorenbos, J. and Pruitt, W.O., 1977. Guidelines for predicting crop water requirements. FAO Irrigation and Drainage Paper 24, FAO, Rome, 144 pp.

[6] Hargreaves, G.L., Hargreaves, G.H. and Riley, J.P., 1985. Irrigation water requirements for Senegal River Basin. *Journal of Irrigation and Drainage Engineering, ASCE*, **111(3)**, 265-275.

[7] Hargreaves, G.H. and Allen, R.G., 2003. History and evaluation of Hargreaves evapotranspiration equation, *Journal of Irrigation and Drainage Engineering, ASCE,* **129(1)**, 53-63.

ISBN: 978-960-6865-94-7

[8] Jensen, M. E., Burman, R. D. and Allen, R. G. (eds), 1990. Evapotranspiration and Irrigation Water Requirements. ASCE Manuals and Reports on Engineering Practices No 70, ASCE, New York, 360 pp.
[9] Papazafiriou Z., 1999. Crop water requirements. Publisher ZITI, pp. 347.
[10] Panoras A., Papazafiriou E. and Poultsidou Th., 2001. Estimation of crop coefficient for six relations of evapotranspiration in the southern part of Thessaloniki plan. *Agricultural Research*, **24 (1),** 37-45.
[11] Penman, H. L., 1956. Evapotranspiration: An introductory survey. *Netherland Journal of Agricultural Science*, **4**, 9-29.
[12] Sakellariou Makrantonaki M., Panoras A., Mavroudis I. and Pogiaridis Th., 1996. Distribution maps of daily average reference evapotranspiration and rainfall in prefectures of Karditsa and Trikala. Proceedings of International Scientific Conference on Water Resources Management, November 13-16, Larisa, 1, 232-243.

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Improving efficiency of a water distribution network by implementing a pump as turbine system: Antalya Case Study

I. E. Karadirek, O. Gulaydin, Ö. Özen, A. Muhammetoglu*, H. Muhammetoglu

Department of Environmental Engineering, Akdeniz University, Antalya, Turkey
*Corresponding author: Email: aysemuh@akdeniz.edu.tr

Abstract

Due to aging and deterioration of system components and inefficient management, water losses in water distribution networks (WDNs) are accounted for more than 30% in many countries. One of the main factors causing leakage is pressure where excess water pressure increases the rate of leakage. Consequently, pressure management is the most important and commonly applied action for water losses reduction. A common method to control and reduce pressure and water losses in WDNs is to install a Pressure Reducing Valve (PRV). In recent years, pumps used in turbine mode (Pump as Turbine, PAT) started to appear as a viable option to replace PRVs. In this study, the potential for energy recovery and water losses reduction with the implementation of a PAT system is investigated in a District Metered Area (DMA), namely DMA-16, of Konyaalti WDN in Antalya City, Turkey. DMA-16 covers a residential area where population is expected to increase in the coming years. In this respect, population forecast has been realized for the years 2025 and 2035 and based on the forecasted population values, future water demands and flow rates were estimated. A hydraulic modeling study was conducted to determine the optimum pressure levels to be sustained at the entrance of the DMA. The areal distribution of water pressure and excess water pressure levels were obtained for winter and summer seasons of the years 2025 and 2035 using the hydraulic model predictions. The estimated excess water pressures were between 14.50-17.04 m heads for the mentioned seasons and years. As there is excess water pressure in the studied DMA, then there is potential for implementation of a PAT system at the entrance of the DMA. The benefits of installing a PAT system were investigated where the average of potential power production was between 0.97 and 1.36 kWh and the average water losses reduction was between 2.72 and 4.04 m^3/h. The proposed PAT system is expected to improve the efficiency of the WDN with the estimated benefits but a cost-benefit analysis is needed to compute the pay-back period and to evaluate the additional environmental benefits.

Keywords: *pump as turbine; water distribution network; excess water pressure; energy recovery; water losses reduction.*

1. INTRODUCTION

Due to increasing population in many cities, urban water demand has increased causing a high pressure on water resources. Within the context of sustainable water supply systems, improvement of energy efficiency, reduction of water losses and CO_2 emissions are taken into consideration. Water losses problem in water distribution networks (WDNs) is common in many countries such as Turkey, where the annual non-revenue water (NRW) is about 44% of system input volume (SIV) 1]. The difference between SIV and authorized consumption is defined as water losses while the difference between SIV and billed water consumption is defined as NRW. Water losses consist of

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physical and apparent water losses. Physical water losses result from the holes and cracks of the pipes and valves and from flooding of reservoirs whereas apparent water losses represent the volume of water that is used but not recorded such as illegal water usage, inaccurate water meter readings and data handling errors [2]. Pressure management is an efficient and economically feasible method to reduce physical water losses in WDNs [3, 4]. Therefore, water authorities have started to apply pressure management in order to reduce physical water losses. The problem of water losses is not only a revenue problem but it also results in wasting sources such as energy. Required energy for water abstraction, transmission, treatment and supply for urban and industry represents 2-3% of the global energy consumption and it is reported that implementation of cost-effective actions could reduce at least 25% of this energy consumption [5].

Pressure management in WDNs can be achieved by implementing pressure reducing valves (PRVs). Recent studies showed that micro turbines or pump as turbines (PATs) could be used for pressure reduction but also to recover the excess water pressure to produce energy [6, 7, 8]. Micro turbines have higher capital costs than PATs that prevent them from having a widespread implementation in WDNs. Recently, several research studies were conducted for investigation of using pumps in reverse mode, as hydraulic turbines [5]. PAT systems help to improve efficiency of WDNs by reducing pressure, water losses and pipe failures in addition to energy production at pico or micro scale. In the literature, theoretical, experimental and numerical investigations are presented for possible applications of PAT systems. Moreover, several research studies are focused on design of PATs, analysis of cavitation, force and efficiency, comparison of conventional turbines with PATs and cost analysis for evaluating economic feasibility [9]. There is limited research in the literature for a detailed hydraulic analysis of a WDN to examine the potential for implementation of a PAT system considering the forecasted population and flow rates in the long term. This paper represents an analysis of the potential energy recovery and physical water losses reduction by implementation of a PAT system in a District Metered Area (DMA), namely DMA-16, of Konyaalti WDN in Antalya City, Turkey. For this purpose, projection of population was realized for the years 2025 and 2035 and based on the forecasted population values, future water demands and flow rates were estimated. A hydraulic modelling study was conducted to determine the excess water pressure at the entrance of the DMA for the upcoming years and potential power generation was also calculated.

2. MATERIALS AND METHODS

2.1 Pilot study area

Konyaalti Water Distribution Network (KWDN) is one of the major sub-networks of the Antalya WDN and operated independent of much of the Antalya WDN. KWDN has been divided into 18 DMAs for efficient management of water losses. The region is supplied by raw water extracted from five wells at *Bogacay Pumping Station*. *Hurma Balancing Reservoir* with a capacity of 15000 m^3 is the only such reservoir in KWDN [4, 10]. DMA-16 was chosen as the Pilot Study Area (PSA) to conduct this study. DMA-16 covers a residential area with around 250 service connections and the total length of water mains in the PSA is around 9000 m. There is a SCADA (Supervisory Control and Data Acquisition) station located at the entrance of DMA-16 where continuous online measurements of flow rate and water pressure are conducted at 5-minute time intervals and the measured data are recorded for future use [11]. Figure 1 depicts the main elements, SCADA stations of KWDN and the PSA.

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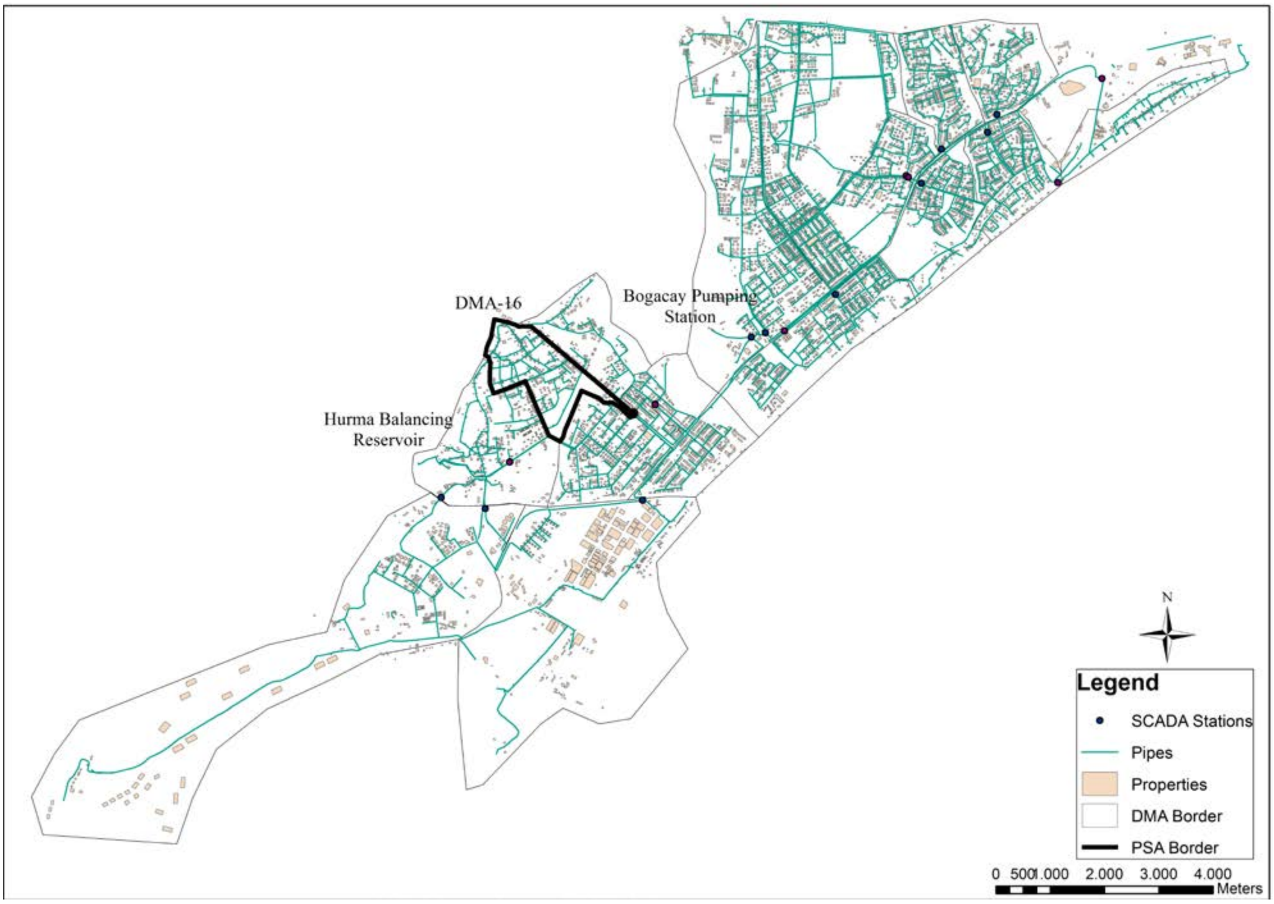


Figure 1. Map showing KWDN, SCADA monitoring stations, Hurma Balancing Reservoir, Pumping Station and DMA-16 (updated from [4])

2.2 Projections of population and water demand

DMA-16 covers a residential area where population is expected to increase in the upcoming years. Within this respect, populations for the years 2025 and 2035 were forecasted. Based on the forecasted population values, future water demands and flow rates were estimated as well. Increase in water demand is assumed the same as population growth rate calculated by Turkish Statistical Institute (TSI) and maximum and minimum water consumption profiles in 2025 and 2035 were calculated by multiplying the observed water consumption profiles in 2010 by the ratio of population increase.

2.3 Hydraulic modelling

In this study, hydraulic modelling of the PSA was conducted using WaterGEMS software with a time step of 5-minute to predict the spatial and temporal changes of water pressures. Details of hydraulic model calibration and verification studies of KWDN including the PSA were given elsewhere [4]. The distribution network simulated for the PSA is depicted in Figure 2. Flow rates and water pressures at the entrance to the PSA were obtained from SCADA system. Flow rates for the years 2025 and 2035 were forecasted based on the projections of population. No change in water pressures over the years at the entrance to the PSA was assumed in this study. Excess water pressure in WDNs is one of the major factors resulting in leakage. Leakage resulted from pipe

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bursts can be defined as a discharge through an orifice. Emitter coefficients can be used to simulate leakage in WDNs [12]. Leakage estimation from a node is possible by application of emitter coefficients in hydraulic modelling. In this study, hydraulic model was used to estimate leakage by application of the following equation:

$$q=C.P^{\gamma} \tag{1}$$

where; P is the nodal pressure, C is the emitter coefficient, q is the flow rate, γ is pressure exponent.

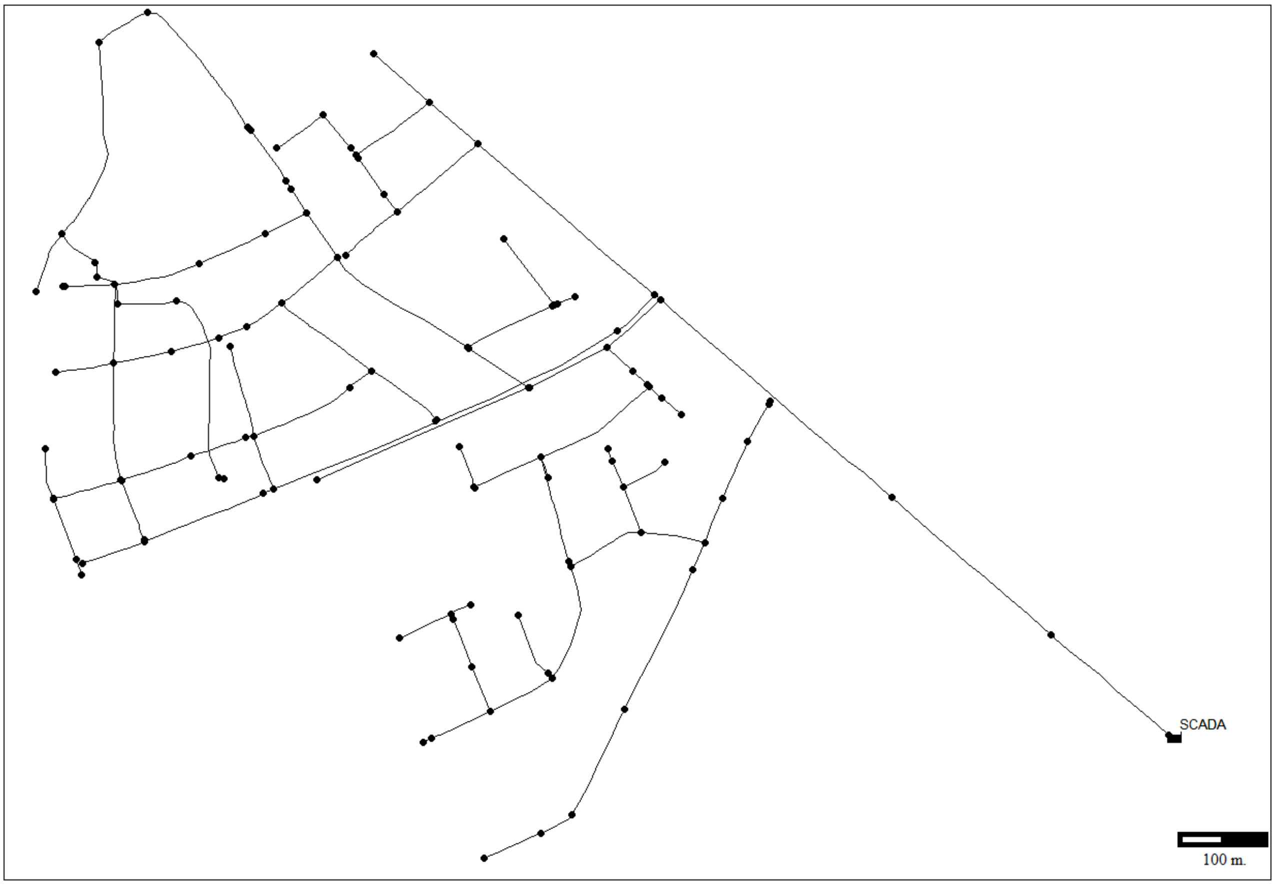


Figure 2. Detailed WDN of the PSA

2.3 Recovery of excess water pressure

Excess water pressure in WDNs can be recovered by application of turbine or PAT systems. Power generation from recovery of excess water pressure can be calculated by the following equation:

$$P = Q.\rho.g.H.e_o \tag{2}$$

where: P is the produced power (watt), Q is flow rate (m^3/s), ρ is water density (kg/m^3), *g* is the acceleration due to gravity (m/s^2), *H* is excess water head (m), and e_o is the efficiency of system.

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3. RESULTS AND DISCUSSION

3.1 Population projection and water demand estimation

Population projection for Antalya city was accomplished with arithmetic, geometric and semilog projection methods by using present and past population records starting from 1935. The estimation results showed good agreement with the estimated population growth rate by Turkish Statistical Institute. Therefore, the annual growth rate of population in the PSA was estimated at 30‰. Increase in water demand was assumed as same as population growth rate for Antalya city. By analyzing the available on-line measurements of flow rate at the SCADA station, located at the entrance of the PSA, the maximum and minimum flow rates were observed in summer (July 20-21, 2010) and winter (December 1-2, 2010) seasons, respectively. Estimated water demands for the years 2025 and 2035 for the minimum and maximum consumption periods are illustrated in Figures 2a and 2b.

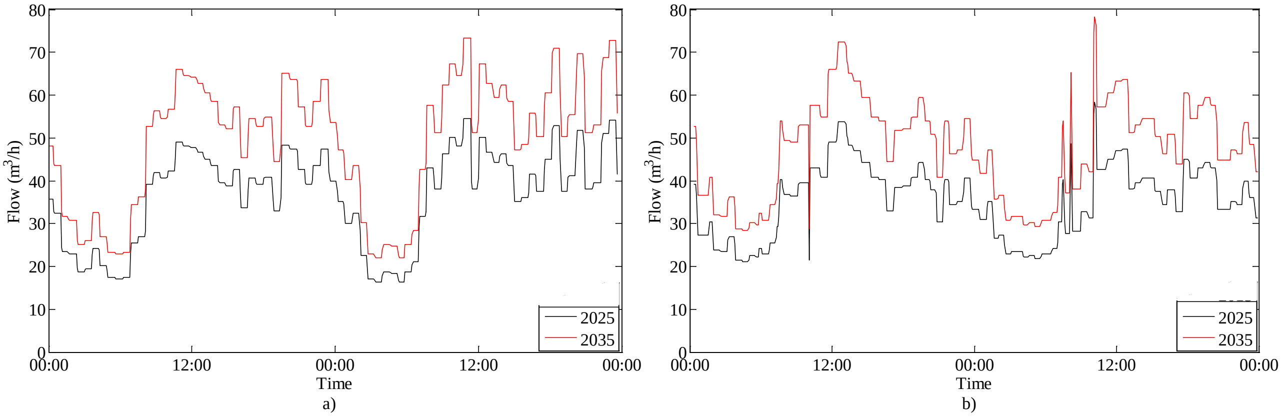
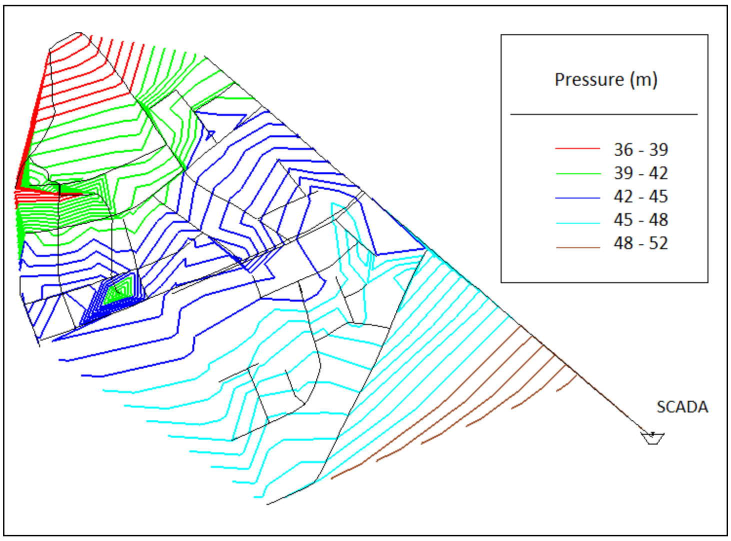


Figure 2. Estimated 48-hour water profiles for the PSA,
a) maximum consumption (summer season), b) minimum consumption (winter season)

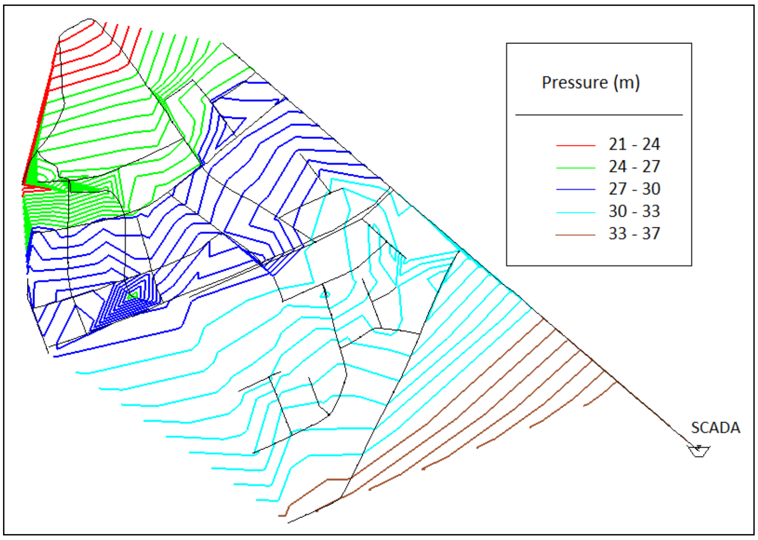
3.2 Pressure management and prediction of water savings due to pressure reduction

Pressure modelling of the PSA indicated that there is excess water pressure in the PSA at all times, including the periods of maximum and minimum flow rates. Average water pressures at the entrance to the PSA for maximum and minimum consumption periods in 2010 were recorded as 51.40 m, and 52.44 m water head, respectively. Therefore, a series of water pressure reduction scenarios were tested to determine optimum water pressure at the entrance to the PSA. The strategy was to maintain a minimum water pressure level of about 20 m water head at all the nodes of the PSA at the maximum and minimum flow rates for the years 2025 and 2035. Temporal and spatial changes of water pressure for each scenario were predicted and spatial changes of water pressures in the PSA for the year 2035 are illustrated in Figure 3, as an example.

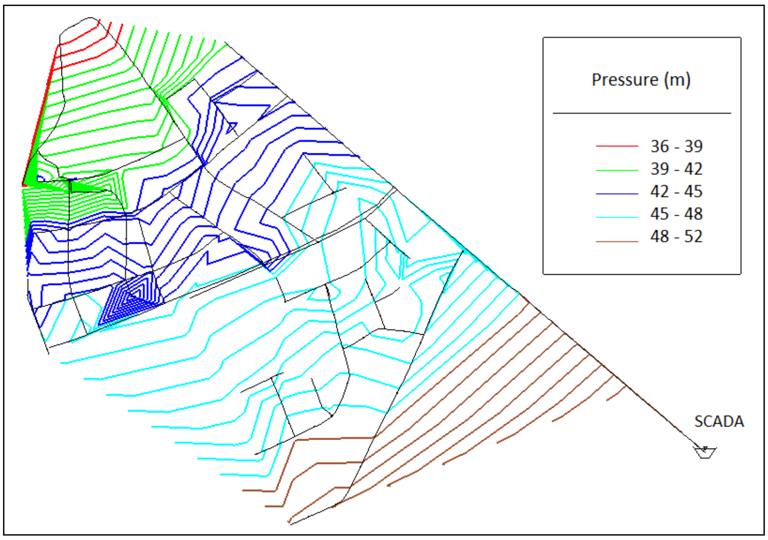
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a)

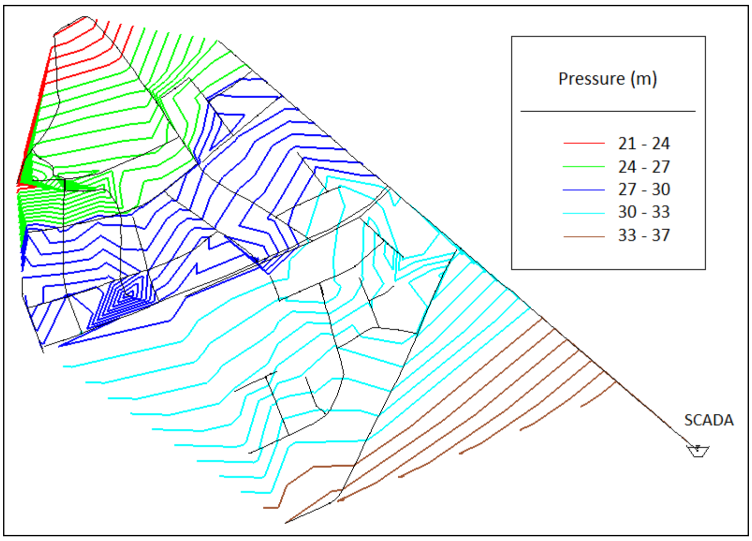


b)



c)

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d)

Figure 3. Prediction of spatial changes of water pressure for the year 2035 a) At minimum flow rate before reducing water pressure , b) At minimum flow rate after reducing water pressure, c) At maximum flow rate before reducing water pressure, d) At maximum flow rate after reducing water pressure

Leakage simulations and water saving predictions for each scenario were generated. Eighty percent of the minimum night flow was accepted as real losses in the PSA [4]. The emitter coefficients were calculated through a trial and error method for each scenario. Estimated optimum water pressures at the entrance to the PSA, predicted water savings and calculated emitter coefficients for each scenario are summarized in Table 1.

3.3 Potential power generation by reducing excess water pressure

Excess water pressure is the difference between water pressures upstream and downstream of the pressure reducing valve/tank. Excess water pressure can be converted into energy to produce electricity if a turbine/PAT system is installed. Potential power generation was calculated for each scenario in case of installation of PAT/turbine system to reduce excess water pressure at the entrance of the PSA. For this purpose, overall system efficiency was accepted as 70%. For each scenario, the optimum pressure heads at the entrance of the PSA were predicted by the hydraulic model. Decrease in flow rates due to pressure reduction in the PSA was also considered and estimated by the hydraulic model. The calculated average power generation from each scenario is presented in Table 1. Estimated potential power generations, for minimum and maximum consumption periods and all years, are illustrated in Figure 4.

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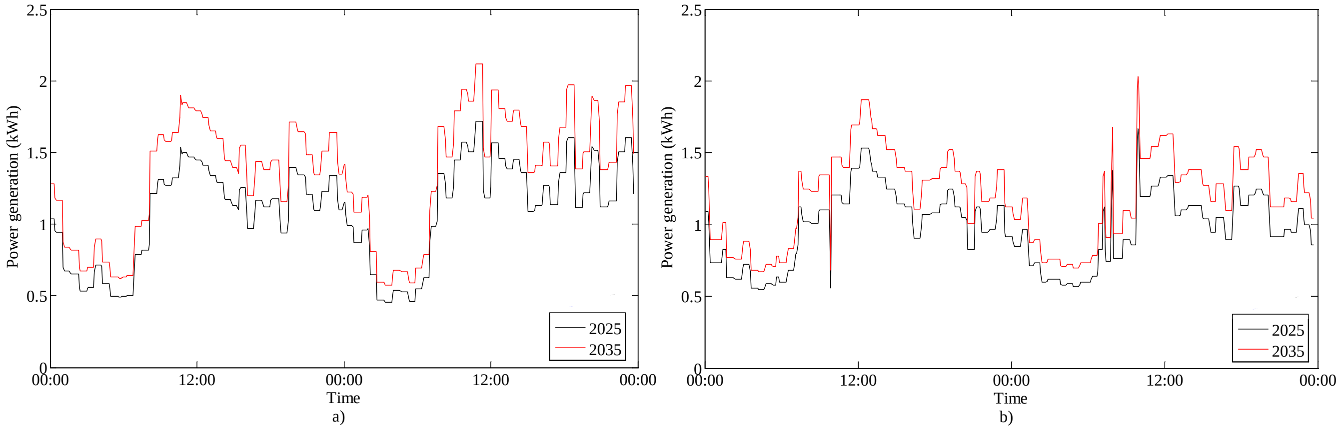


Figure 4. Predicted potential power generation from the system a) maximum consumption (summer season), b) minimum consumption (winter season)

Table 1. Summary of pressure management scenarios for the PSA

Year	Period	Emitter coeff.	Flow[1] (m^3/h)	Flow[2] (m^3/h)**	Ave. water pressure (m)	Opt. water pressure (m)	Excess water pressure (m)	Ave. power generation (kWh)	Ave. water saving (m^3/h)
2025	Min.	0.0222	35.30	31.91	51.40	35.40	16.00	0.97	3.39
	Max.	0.0168	36.56	33.84	52.44	35.40	17.04	1.10	2.72
2035	Min.	0.0295	47.05	43.01	51.40	36.90	14.50	1.19	4.04
	Max.	0.0230	49.34	45.97	52.44	36.90	15.54	1.36	3.37

Flow[1]: Predicted flow rate at the entrance to the PSA, Flow[2]: Predicted flow rate at the entrance to the PSA after pressure reduction. "Min." refers to the minimum consumption period, while "Max." stands for maximum consumption period.

4. CONCLUSIONS

Excess water pressure causes increase in physical water losses and the frequency of pipe bursts. Therefore, improving hydraulic efficiency of WDNs is vital for such cases. This study showed that reducing water pressure resulted in a considerable decrease in physical water losses while producing power by implementation of a PAT system. Implementation of PAT systems helps to improve efficiency of WDNs by reducing pressure, water losses, frequency of pipe bursts and CO_2 emissions in addition to energy production at pico or micro scale. Water demands exhibit significant changes during the service life of WDNs. Hydraulic models are effectively used to predict flow rate and pressure levels in WDNs and these predictions are very helpful to estimate optimal network pressure and excess pressure levels. In this study, changes in water demands were considered for hydraulic modelling to predict excess water pressure, power generation and water savings. For further studies, it is recommended that a cost-benefit analysis should be carried out to calculate the pay-back period and to evaluate the additional environmental benefits.

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References

[1] Turkish Statistical Institute Water Statistics of Municipalities [online] Available at: http://www.tuik.gov.tr/PreHaberBultenleri.do?id=16171 (accessed: 7 December 2014).

[2] Lambert, A., Brown, T., Takizawa, M., Weimer, D., 1999. Review of Performance Indicators for Real Losses from Water Supply Systems. *J. Water Supply: Res. T.-AQUA*, 48, 227-237.

[3] McKenzie, R., Lambert, A. 2002 Economic model for leakage management for water suppliers in South Africa, *WRC Report* TT 169/02. http://www.wrc.org.za/Other%20Documents/Software/econoleak/TT%20169-02.PDF Accessed: 07.12.2015

[4] Karadirek, I.E., Kara, S., Yilmaz, G., Muhammetoglu A., Muhammetoglu, H. 2012. Implementation of hydraulic modelling for water-loss reduction through pressure management. *Water Resour Manage*, 26(9), 2555-2568.

[5] DeMarchis, M., Fontanazza, C.M., Freni, G., Messineo, G., Milici. B., Napoli, E., Notaro, V., Puleo, V., Scopa, A., 2014. Energy recovery in water distribution networks. Implementation of pumps as turbine in a dynamic numerical model, *Procedia Engineering*, 70:439-448.

[6] Carravetta, A., Del Giudice, G., Fecarotta, O, Ramos, H.M., 2012. Energy Production in Water Distribution Networks: A PAT Design Strategy, *Water Resour Manage*., 26:3947–3959.

[7] Fontana, N., Giugni, M., Portalano, D., 2012. Losses Reduction and Energy Production in Water-Distribution Networks, *Journal of Water Resources Planning and Management*, 138: 237-244.

[8] Fecarotta, O., Aric`o, C., Carravetta, A., Martino, R., Ramos, H.M. 2015. Hydropower Potential inWater Distribution Networks:Pressure Control by PATs, *Water Resour Manage*., 29:699–714

[9] Jain, S.V., Patel, R.N. 2014. Investigations on pump running in turbine mode: A review of the state-of-the-art, *Renewable and Sustainable Energy Reviews*, 30: 841–868.

[10] Karadirek, I.E., Kara, S., Muhammetoglu, A., Muhammetoglu, H., Soyupak, S., 2015. Management of chlorine dosing rates in urban water distribution networks using online continuous monitoring and modeling, *Urban Water Journal*, DOI: 10.1080/1573062X.2014.992916.

[11] Kara, S., Karadirek, I.E., Muhammetoglu, A., Muhammetoglu, H., 2015. Real time monitoring and control in water distribution systems for improving operational efficiency, *Desalination and Water Treatment*, DOI: 10.1080/19443994.2015.1069224.

[12] Rossman, L.A., 2000. EPANET 2 Users Manual. National Risk Management Research Laboratory, Office of Research and Development , USA EPA, Cincinatti, OH 45268, 29–90

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Agricultural nitrate pollution of groundwater in Antalya – Turkey

A. Çil, R. Keyikoğlu, F. Yenilmez, A. Muhammetoglu, H. Muhammetoglu*

Department of Environmental Engineering, Akdeniz University, 07058, Antalya, Turkey.
**Corresponding author: Email: muhammetoglu@usa.net*

Abstract

Diffuse agricultural nitrate pollution of groundwater is a common serious problem faced by many undeveloped, developing and developed countries due to the excess application of chemical and organic fertilizers. Excess nitrate levels in water, beyond certain limits, inhibit the use of water for drinking purposes. On the other hand, removal of nitrate needs complex and expensive treatment process. Therefore, nitrate pollution should be monitored, assessed and managed to protect groundwater resources. The aim of this research study is to assess the risk of groundwater to nitrate pollution in karstic regions. Altinova agricultural region was chosen as a pilot study area (PSA) to apply this study. Most of the PSA has karst formation characterized by underground drainage systems with sinkholes, dolines, and caves. Intensive agricultural activities in the form of greenhouses for many crops such as tomatoes, eggplants, pepper, and flowers are widely practiced in the PSA. Seasonal field and lab studies were conducted at 25 sampling and measurement points for one year in 2015 and 2016. Water quality parameters such as nitrate, electrical conductivity, salinity, pH, total dissolved solids were investigated in addition to depth to groundwater, and soil characteristics. The results showed wide variations of nitrate concentrations from below 2.0 mg NO_3 per liter to above 100 mg NO_3 per liter. High nitrate concentrations were usually associated with relatively high electrical conductivity levels, exceeding 550 µS cm^{-1}. The geological and hydrogeological characteristics of the PSA and the pollution loads were also investigated to assess vulnerability of the PSA to pollution and hazards. Depth to groundwater ranged between around 15 m to 40 m. Net recharge was estimated at 551 mm $year^{-1}$ while hydraulic conductivity is evaluated at 864 mm day^{-1}. Vulnerability analyses of pollution to groundwater showed that most of the PSA has high vulnerability to pollution.

Keywords: Antalya; groundwater; nitrate; karst; agriculture; vulnerability

1. INTRODUCTION

Karst aquifers are among the most important water resources for drinking, irrigation and industrial water all over the world. Karst aquifers are particularly vulnerable to pollution mostly because of thin soils, and flow concentration in the epikarst (the top, usually severely fractured and karstified layer of a karst aquifer) and recharge by swallow holes where pollutants can simply reach the groundwater and be transported rapidly in karst channels for long distances [1, 2]. As a result, karst aquifers are usually vulnerable to pollution and they need careful management to protect them.

The increasing demand of groundwater resources and disposal of contaminants cause serious challenges in management and protection of groundwater quality. Protection of karst aquifers against contamination requires certain preventive measures. Agricultural activities are among the most important pollution sources causing adverse environmental impacts and contamination in karst groundwater. Especially, agricultural diffused agrochemicals and organic pollution sources are more extended and difficult to control. The intensive use of agricultural fertilizers and pesticides

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has been one of the major issues in agricultural development due to their contribution to high yields but they usually highly deteriorate groundwater quality. In recent years, the increase in the population caused a high increase in agricultural activities. This situation triggered the excess use of synthetic fertilizers and pesticides. Consequently, they resulted in important environmental problems like nitrate contamination in groundwater [3, 4]. There have been lots of places and scientific studies related with this problem widely spread all around the world [5, 6, 7, 8].

One of the most intense agricultural areas in Turkey is Antalya-Altinova region located in Antalya city of Turkey. The area is characterized by karstic hydrogeological structure. In this study, agricultural nitrate pollution of groundwater resources in the area of Altinova was assessed. For this purpose, seasonal in-situ measurements and lab studies were conducted at 25 sampling locations in 2015 and 2016. The temporal and spatial variations of water quality parameters such as nitrate, electrical conductivity, salinity, pH, total dissolved solids were investigated together with depth to groundwater.

2. MATERIALS AND METHODS

2.1 Description of the pilot study area

The pilot study area (PSA) of Altinova region is approximately 10 km far from Antalya City center and covers an approximate area of 75 km^2 overlying a travertine plateau at an altitude of 80 m above mean sea level on the average. The location of the PSA is shown in Figure 1. The PSA is mainly used for agricultural activities but residential buildings also exist in the PSA. The high permeability of the karst aquifers in Altinova region could be regarded as a positive aspect regarding recharge to groundwater but it increases the vulnerability of the underlying groundwater to pollution. There has been a fast intensive agricultural development in the region during the last decade that agricultural land and greenhouses occupied most of the area. The main planted crops are flowers and vegetables such as tomato, cucumber, eggplant, and pepper. Groundwater wells are the main source for irrigation water in the area.

The pervasive pollutants in the PSA are agrochemicals and fertilizers. Besides, the PSA lacks a sewage collection system. Up to present time, domestic wastewater from residential areas of the PSA is disposed of into percolating septic tanks drilled and constructed into the travertine. On the travertine plateau, high rates of precipitation and surface runoff is expected to penetrate through the ground due to the fissured and soluted channels. Drinking groundwater wells located in the PSA were abandoned by Antalya Water and Wastewater Administration (ASAT), as the quality of the groundwater has been deteriorated, especially for nitrate, and became unsuitable for human consumption.

Main geologic formations of the study area are mesozoic aged limestones and marls. Miocene aged aquatic limestones, marls, silty clay deposits, sandstones and conglomerates also exist in the area. There are a lot of karst features such as sinkholes, dolines, caves, poljes, solution cavities, karst springs and similar features in travertines which widely covers the Miocene aged old units [9]. Travertine deposits have been subjected to karstification processes after they had formed which has led to the formation of karstic springs and groundwater system in the travertine deposits [10]. The travertine plateau, which covers the study area, bounded by the Aksu River basin at the east, Beydağları Mountain at the northwest and Antalya Bay at the south, is considered to be the largest known deposits in the world [2].

Typical Mediterranean climate which is warm and rainy in the winter, hot and dry in the summer prevails in the PSA. Vegetation cover of the area is composed of small trees and dense bushes called macchie. The mean annual gross precipitation is 1240.09 mm/year while the mean annual temperature is 19.24 °C, according to the data sets obtained from the nearest meteorological station to the PSA between the years 2000 and 2015.

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Figure 1. Location of Altinova study area in Antalya and Turkey

2.2 Field measurements and data collection

A total of 25 representative irrigation groundwater wells were chosen for monitoring the groundwater quality in the PSA. The locations of the monitored groundwater wells and the geological formation at the wells are presented in Figure 2.

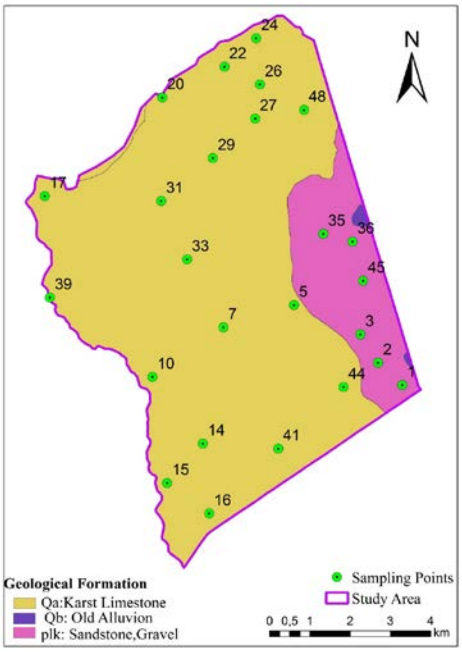


Figure 2. Geological formation and sampling points at the study area

Three sessions of seasonal in-situ measurements in August 2015, November 2015 and February 2016 were conducted at the selected groundwater wells for the measurements of temperature, salinity, electrical conductivity, pH, total dissolved solids, turbidity, dissolved oxygen and nitrate concentrations. The measurements were realized using multi-parameter measurement equipment (HACH HQ40d), a turbidimeter (HACH 2100Q) and a nitrate electrode. Nitrate concentration was also measured in the lab using standard methods for the analyses of water and wastewater [11]. Moreover, depth to groundwater at the selected wells was measured in November 2015 and February 2016 measurement seasons.

In addition to field measurements, routine site surveys were conducted to collect important data sets regarding the agricultural activities such as type of planted crops and their yearly yields, type and amount of applied fertilizers and pesticides, source and amount of irrigation water. Also, pollution sources other than the agricultural activities were determined during the site surveys. Moreover, data sets for rainfall intensity, temperature, and evaporation rates were collected from the closest meteorological station to the PSA

2.3. Water quality sampling and analyses

One session of intensive water quality sampling and analyses was realized in November 2015 at all the selected wells. Water quality analyses were conducted for bacteriological and chemical parameters including residuals of pesticides. The investigated bacteriological parameters were *Escherichia coli*, enterococci, and coliforms while many chemical parameters were analyzed such as nitrate, nitrite, poly aromatic hydrocarbon (PAH), selenium, aluminium, ammonium, chloride, color, Fe, Mn, odour, sulphate, sodium, total organic carbon, arsenic, benzene, boron, bromate, heavy metals, and fluoride. Residuals of pesticides were analyzed for organochlorine pesticides (HCB, alpha-HCH, gamma-HCH, heptachlorine, heptachlor epoxide, aldrin, dieldrin, alpha-endosulfan, beta- endosulfan, total DDT), organophosphorous pesticides (Demethon(O+S), azinphos-methyl, azinphos-ethyl, diazinon, disulfoton, ethion, malathion, parathion-ethyl, parathion-methyl, methamidophos, chlorpyriphos-ethyl, chlorpyriphos-methyl), herbicides (atrazine, simazin), carbamates (aldicarb, aldicarb-sulfone, aldicarb-sulfoxide, carbaryl, carbofuran, carbofuran-3-hydroxy, methiocarb, methomyl, 1-naphtol, oxamyl, propoxur). All the water quality analyses were conducted by the accredited Antalya Public Health Laboratory which belongs to the Turkish Republic Ministry of Health.

2.4. Soil sampling and analyses

A total of 25 soil samples were collected from the top soil very close to the selected monitoring groundwater wells. The collected soil samples were analyzed once in November 2015 for soil texture, pH, salinity, electrical conductivity, organic content, total N, nitrate N, ammonium N, infiltration rate and bulk density.

3. RESULTS AND DISCUSSION

3.1. Results of the field measurements

The statistical evaluation of the monitoring results of the conducted three sessions of field measurements is presented in Table 1. Moreover, the spatial distribution maps for specific conductivity, nitrate in summer (August 2015) and winter (February 2016) and depth to groundwater are presented in Figures 3-5. The maps were created using ArcGIS 10.2 software and ordinary kriging method, which is one of the widely used geostatistical method.

The results showed very marginal temporal variations of the main investigated parameters such as nitrate, conductivity and depth to groundwater. For example, the mean concentrations of nitrate investigated in the three measurement sessions ranged between 44.98 and 46.37 mg/L while the mean levels of specific conductivity ranged between 405.96 and 411.48 µS/cm.

The mean depth to groundwater investigated in November 2015 and February 2016 were 28.19 and 28.58 m. On the other hand, the PSA showed wide spatial variations for the main investigated parameters. e.g. nitrate concentrations ranged from below 1.0 mg/L to above 120 mg/L. Also, specific conductivity ranged from 252 to 599 µS/cm while depth to groundwater ranged from 12.24 m to 43.12 m. High nitrate concentrations were usually associated with relatively high electrical conductivity levels. In general, the northern part of the PSA area exhibited relatively low nitrate and conductivity values.

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Table 1. Statistical evaluation of the field measurements in the years 2015 and 2016

	1st Field Study (August 2015)				2nd Field Study (November 2015)				3rd Field Study (February 2016)			
	Mean	**Std. Dev.**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Min**	**Max**
Temperature (°C)	21.48	1.14	19.80	24.00	19.56	0.92	18.00	21.20	19.08	0.93	17.70	21.10
pH	6.87	0.19	6.44	7.12	7.24	0.11	7.06	7.54	7.18	0.09	7.03	7.39
Specific conductivity (μS/cm)	405.96	93.45	252.00	576.00	414.64	98.08	261.00	593.00	411.48	99.47	256.00	599.00
DO (mg/L)	7.16	2.34	1.94	9.05	7.40	2.00	2.01	9.18	7.20	2.00	2.36	9.05
Salinity (‰)	0.19	0.05	0.12	0.28	0.20	0.05	0.12	0.29	0.20	0.05	0.12	0.29
Turbidity (NTU)	2.01	1.86	0.33	7.68	1.74	3.32	0.32	16.20	4.20	5.51	0.37	22.30
TDS (mg/L)	195.72	45.98	120.20	279.00	200.04	48.33	124.70	288.00	198.38	48.96	122.40	291.00
Nitrate (mg/L)	45.68	32.94	0.33	128.30	44.98	30.14	0.25	98.56	46.37	32.66	0.59	108.70
Depth to groundwater (m)					28.19	9.34	13.76	42.60	28.58	9.93	12.24	43.12

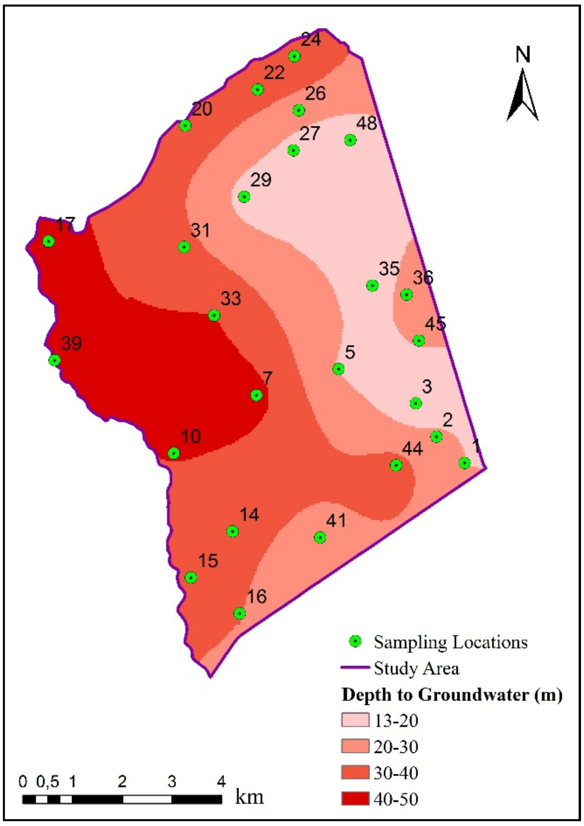
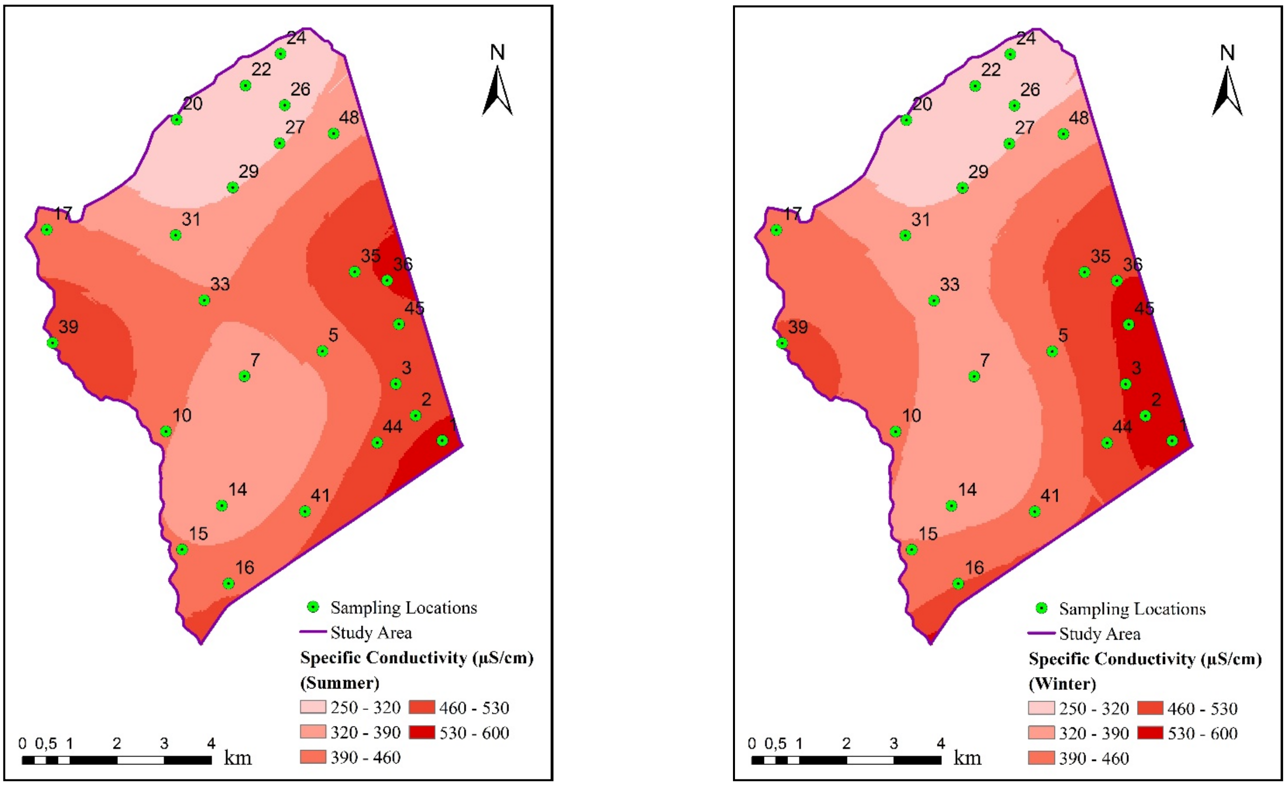


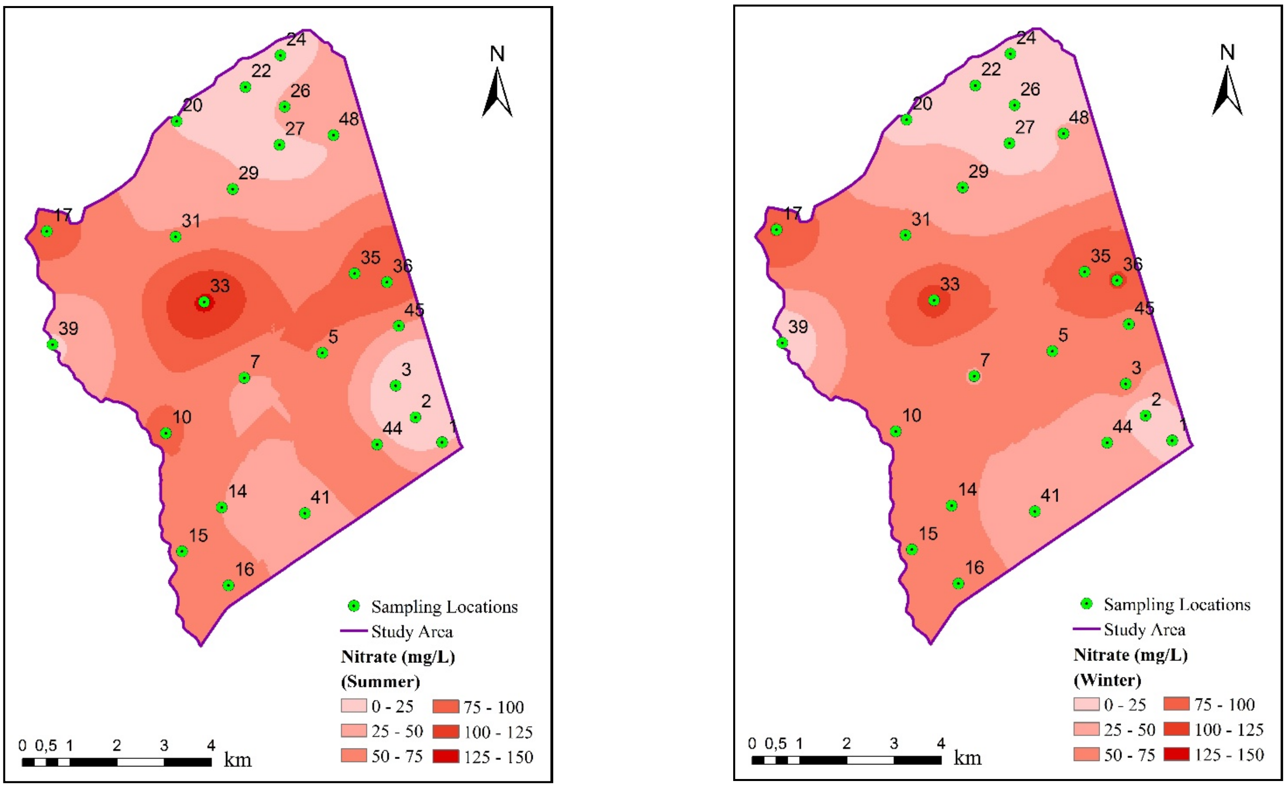
Figure 3. Spatial distribution of depth to groundwater

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(a) Summer (b) Winter

Figure 3. Spatial distribution of specific conductivity values



(a) Summer (b) Winter

Figure 4. Spatial distribution of nitrate concentration values

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Results of the groundwater and soil analyses

Basic statistical summary of the bacteriological and chemical analyses results of groundwater, conducted in November 2015, is presented in Table 2. All the investigated residuals of pesticides concentrations were below the detection limit. A number of groundwater wells were polluted with coliform bacteria including *Escherichia coli* which are originated from human sewage. This is because the PSA lacks a sewage collection system where percolating pits are used to dispose of sewage. Moreover, iron, manganese and arsenic levels at some wells were higher than the permissible limits for drinking purposes according to the Turkish standards [12].

Table 1. Basic statistical summary of the groundwater quality analyses results in November 2015

Parameters	Permissible Limit	Min	Max	Mean	Std. Dev.
Coliform Bacteria (cfu/100 mL)	0	0.000	1300.000	127.400	309.743
Total Viable Count(cfu/mL)	-	0.000	1500.000	88.880	300.513
C,perfringens (cfu/100 mL)	0	0.000	3.000	0.200	0.645
Enterococci (cfu/100 mL)	0	0.000	24.000	2.760	6.495
Escherichia coli (cfu/100 mL)	0	0.000	14.000	0.880	2.848
TOC (mg/L)	-	0.410	1.340	0.965	0.219
Iron (μg/L)	<200	7.325	379.005	46.326	89.404
Boron (mg/L)	<1	0.007	0.143	0.033	0.040
Mercury (μg/L)	<250	0.022	0.056	0.029	0.011
Chromium (μg/L)	<50	2.106	6.356	3.297	0.939
pH	6.5-9.5	7.000	7.450	7.188	0.106
Nickel (μg/L)	<20	1.792	6.755	2.918	1.010
Lead (μg/L)	<10	0.026	0.208	0.055	0.048
Manganese (μg/L)	<50	0.259	66.376	4.137	13.216
Sodium (mg/L)	<250	4.610	25.404	12.212	5.896
Arsenic (μg/L)	<10	0.274	38.763	3.560	7.534
Selenium (μg/L)	<10	0.134	0.926	0.287	0.196
Aluminium (μg/L)	<200	2.385	71.369	11.646	16.785
Sulphate (mg/L)	<250	3.260	139.680	30.730	34.183
Ammonium (mg/L)	<0.5	0.020	0.070	0.044	0.013
Bromate (μg/L)	<10	0.010	0.010	0.010	0.000
Chloride (mg/L)	<250	7.620	50.280	20.340	11.991
Nitrate (mg/L)	<50	0.060	118.480	44.775	32.197
Fluoride (mg/L)	<1.5	0.030	0.160	0.061	0.036
Nitrite (mg/L)	<0.5	0.010	0.050	0.012	0.008

Soil analyses results showed that all the samples are mostly clay soils with low alkalinity and salinity. The infiltration rates were slow or medium level. Most of the samples showed good levels of total nitrogen but the organic contents were low in general.

4. CONCLUSIONS

Karst aquifers are crucial water resources for domestic and irrigation water supply in Turkey but these limited and vulnerable water resources require special protection and management. Most of the groundwater quality in the Pilot Study Area (PSA) of Altinova has been deteriorated with high

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concentrations of nitrate due to the excess application of agrochemicals. The nitrate concentrations at many of the investigated groundwater wells in the PSA exceeded 50 mg/L which is the upper limit given in the Regulation Concerning Water Intended for Human Consumption. Moreover, *Escherichia coli* were detected at a number of groundwater which implies contamination of groundwater with sewage. The PSA showed marginal temporal variations of nitrate pollution but the spatial variation was very wide ranging from levels below 1.0 mg/L to above 120 mg/L. High levels of nitrate were usually associated with high levels of electrical conductivity. The conducted research study shows that there is an urgent need for integrated management of groundwater quality in the PSA. Well coordinated and integrated actions for management of water, land and human activities are required to achieve environmental, social and economic welfare in an equitable manner without compromising the further deterioration of valuable water resources.

References

[1] Mimi, Z.A. and Assi, A. 2009. Intrinsic vulnerability, hazard and risk mapping for karst aquifers: A case study", *Journal of Hydrology*, **364**, 298–310.

[2] Özyurt, N.N. 2008. "Residence time distribution in the Kirkgoz karst springs (Antalya-Turkey) as a tool for contamination vulnerability assessment", *Environ Geol*, **53**, 1571–1583.

[3] Muhammetoglu, H., Muhammetoglu, A., Soyupak, S. 2002. Vulnerability of Groundwater to Pollution from Agricultural Diffuse Sources: A Case Study, *Water Science and Technology*, **45(9)**, 1-7.

[4] Muhammetoglu, A. and Uslu, B. 2007. Application of environmental impact quotient model to Kumluca region, Turkey to determine environmental impacts of pesticides, *Water Science and Technology*, **56(1)**: 139–14.

[5] Power, J.F. and Schepers, J.S. 1989. Nitrate contamination of groundwater in North America. Agriculture, *Ecosystems and Environment*., **26(3-4),** 165-187.

[6] Johnson, C. J. and Kross, B. C., 1990. Continuing importance of nitrate contamination of groundwater and wells in rural areas, *American Journal of Industrial Medicine*, **18(4)**, 449–456.

[7] Suthar, S., Bishnoi, P., Singh, S., Mutiyar, P. K., Nema, A. K. and Patil, N. S. 2009. Nitrate contamination in groundwater of some rural areas of Rajasthan, India, *Journal of Hazardous Materials*, **171(1-3)**, 189-199.

[8] Su, X., Wang, H., Zhang, Y. 2013. Health Risk Assessment of Nitrate Contamination in Groundwater: A Case Study of an Agricultural Area in Northeast China, *Water Resources Management*, **27(8),** 3025-3034.

[9] İnan, N. 1985. *Antalya Travertenlerinin Oluşumu ve Özellikleri*. Cumhuriyet Üniv. Jeoloji Müh. Böl. Yayınları, Sivas. (In Turkish)

[10] Efe, R., Atalay, İ., Soykan , A., Cürebal, İ., & Sarı, C. 2008. *The Formation of Antalya Travertine Deposit and Karstic Ground Water Systems*. Environment and Culture in the Mediterranean Region. Part I, Chapter Six, 93-108.

[11] APHA, AWWA, WEF. 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed., Washington, DC: APHA.

[12] Ministry of Health. 2013. *Regulation Concerning Water Intended for Human Consumption*, Turkey. Official Gazette, Date: 7 March 2013, Issue: 28580.

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Restoring the River Niger

R. I. Enang

Water Engineering and Development Centre (WEDC), School of Civil and Building Engineering, Loughborough University, Epinal way, Loughborough. LE11 3UE.
Email: r.i.enang@lboro.ac.uk

Abstract

The River Niger is the third longest river in Africa and this comes with high demands from raw water supply to agriculture and other livelihoods. This river located in West Africa passes through diverse climate regions on its way to the sea including areas prone to desertification; and although it is a transboundary river, there isn't much global interest in it and therefore much importance isn't placed on preserving the nature and quality of the river. This paper incorporates information found on various databases in form of research conducted at strategic locations along the course of the river, from source to delta, and on its major tributaries. It uses this information as data to map man-made disturbances and its interaction with the environmental conditions and shows their gradual cumulative effects along the course of the river. It also reveals their contribution to the changing natural course of the river, the further impacts downstream and on the river behaviour at the delta before entering the sea. It outlines disturbances including contaminated tributaries from rural areas, treated and untreated wastewater disposal, heavy metal from catchment runoff, infrastructures and other restrictions on the river's flow path and their interaction with the geology, climate and hydrochemical properties of the stream and finally shows ways to mitigate these disturbances, with reference to and lessons learnt from the actions and action plans from African intergovernmental partnerships and other river governing and monitoring bodies such as the Nile Basin Initiative.

Keywords: River Niger; industrial wastewater; damming; contaminated tributaries; irrigation.

1. INTRODUCTION

The River Niger originates from the highlands of Guinea and flows into the North Atlantic Ocean, passing through Guinea, Mali, Niger, Benin (Northern border), and entering the ocean at the Niger Delta in Nigeria. River Niger (R. Niger) straddles through six countries but its river basin encloses nine countries including Algeria, Burkina Faso, Cote d'Ivore and Cameroun, drained either by R. Niger itself or one of its major tributaries [[1]]. 50% of the R. Niger's drainage basin is subject to the harsh conditions of the Sahel Climate region, with effects such as drought and desertification. Being a source of livelihood to millions of people, anthropogenic activities on its course and on major tributaries choke the river and with over 70% of the rural population relying on natural resource based livelihoods; chronic and acute pollution changes the quality of the water which is also heavily relied on for drinking [[2]]. There has been significant change in the flow regime and rainfall pattern in the R. Niger Basin over the years [[1]]. Changes in the nature of a river though mostly from climatic factors are often traced back to anthropogenic activities. [[3]].

Most fascinations on R. Niger have been on its course, originating just a few miles from the Atlantic Ocean but flowing away towards the Sahara Desert and making a sharp turn to empty into the Atlantic Ocean at the gulf of guinea. Studies have produced a handful of theories over the years, which have evolved into our present knowledge of why the Niger acts the way it does [[4]]. This knowledge along with the drought of 1984 - within the basin - sparked interests in the flow regime

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of R. Niger. Matters of hydrology in the R. Niger have been covered extensively in [[1], [5], [6], and [7]]; these investigations also included the sole and collective hydrological effects of dams on the course of the R. Niger and its major tributaries. Majority of research on anthropogenic activities investigate the environmental conditions of the oil rich Niger Delta [e.g. [8]], while others investigate infrastructures on the river [e.g. [3]] and few on the effects of wastewater [e.g. [9]]. The hydrological impacts are well known therefore this research aims to compile the knowledge of the activities around the R. Niger, in order to understand the sources of non-hydrological stresses on the river. It focused on some of the impacts caused by the activities and living conditions of people in the riparian communities, with reference to more common environmental challenges.

2. METHODOLOGY

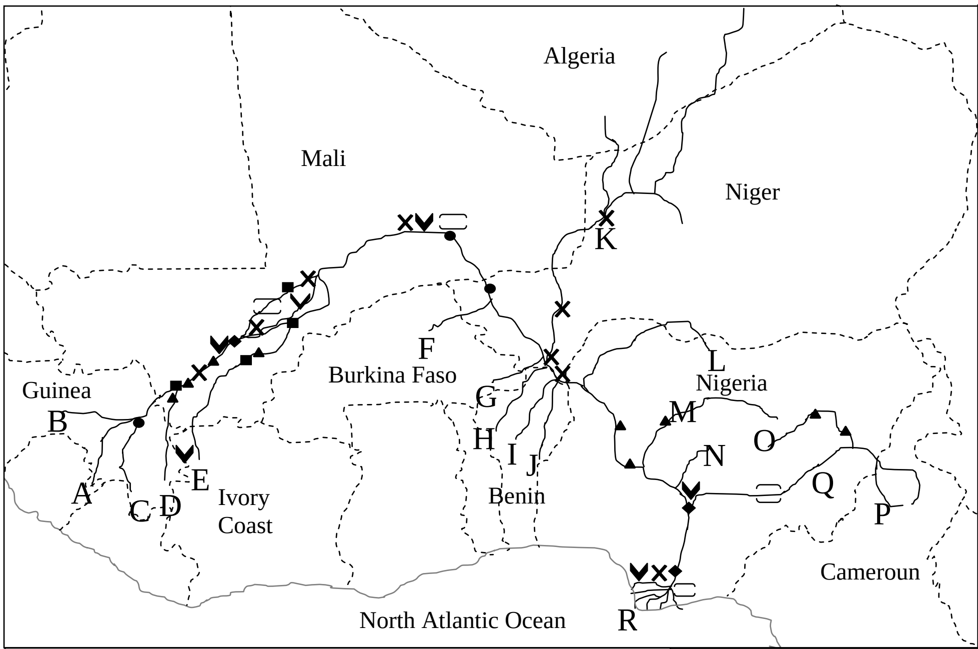
The anthropogenic activities along R. Niger including dams, mining and other human activities were mapped on its course. The location of tributaries helped to approximate the point at which an activity occurs. Following the presence of significant knowledge on hydrologic conditions, this paper assessed the effects of human activities and points to the natural occurrences which stimulate them when necessary. Research was done mostly using academic and non-academic sources. Academic sources however, did not cover in depth the situation at the upper trenches particularly Mali and Niger in which case non-academic sources were employed. Video documentaries on people, culture, livelihoods and devastations along the R. Niger proved particularly useful and provided a virtual tour along the river course from which anthropogenic activities and their effects were detected and recorded [[10]]. News outlets were additional non-academic literature sources for the upper trenches. Extra caution was taken when using this type of source, and activities reported were checked across other news outlets and the accuracy of the information was gauged through consistency across at least three independent outlets. Databases of organisations such as Worldbank, African Development Bank AFDB, and the Food and Agriculture Organisation of the United Nations FAO gave credible light on the hydrology of the Basin, location of infrastructure along the Basin, as well as projects and activities of the Niger Basin Authority NBA. Although these sources often correlated the information from the newspaper articles, further research presented them as in-exhaustive particularly for smaller infrastructure, low-impact projects or projects with medium-impact but long term execution.

2.1 Tributaries

There are three major tributaries of the R. Niger in Guinea – Rivers Niandan, Tinkisso and Milo. In Mali, two main tributaries join the R. Niger – R. Sankarani rising from Guinea and R. Bani rising from Ivory Coast. In Niger Republic, the R. Niger is met by six major tributaries originating from Burkina Faso – Rivers Sirba, Gouroual, Dargol Gouroubi, Diamangou and Tapao. Further downstream R. Niger is joined by a seasonal transboundary river known as Vallee de l’Azaouak (also called Vallee de l’Azhar in southern Mali) which drains part of Southern Algeria, South-Eastern Mali and Northern Niger. At the Benin-Niger border, three rivers join the R. Niger – Rivers Mekrou, Alibori and Sota. Many small rivers join the R. Niger in Nigeria but its main sources of the water in this country are Rivers Sokoto-Rima, Kaduna and Benue, with R. Benue being the largest tributary of the R. Niger. R. Benue originates in the Faro highlands in Cameroun and is joined by the R. Faro before entering Nigeria. One of the main tributaries of the R. Benue is the R. Gongola, joining nearly midway of R. Benue’s course. R. Benue joins the R. Niger at Lokoja on its way flowing southerly, R. Niger then disperses into several distributaries, forming the Niger Delta and entering the Ocean at the Niger Delta [[5], [6], [11]]. These are the main tributaries often referred to when addressing matters of the R. Niger.

3. RESULTS

Some of the impacting occurrences found along the river length happened at defined locations and were mapped out. A lot of them however, occurred very frequently along the river length and mapping them out proved to be of no practical relevance therefore, within this reason, they were assumed to occur along the entire length of the river. Figure 1, maps the location of some occurrences along the River Niger which influence its flow and quality, with respect to some tributaries. It can be seen that majority of the activities occur in the upper reaches in Mali, with some high impact activities in Nigeria and a few in Niger.



A R. Niger at source
B Tinkisso River
C Milo River
D Sankarani River
E Bani River
F Sirba River
G Tapao River
H Mekrou River
I Alibori River
J Sota River
K Vallee de l'Azaouak
L Sokoto-Rima River
M Kaduna River
N Gurara River
O Gongara River
P Faro River
Q Benue River
R R. Niger at Delta

•	Incomplete Dams	v	Mining/Drilling/Mineral
▲	Complete Dams	×	High Evaporation
■	Planned Dams	≈	Flooding

Figure 1. Anthropogenic and Natural Occurrences along River Niger and its major tributaries.

3.1 Dams

On R. Niandan is Fomi Dam, currently under construction, near the confluence of Rivers Niger-Niandan. On R. Sankarani is the Selingue Dam and on R. Bani are two dams: Djenne Dam and Talo Dam. On R. Niger in Mali there are two dams: Sotuba Dam downstream of Rivers Niger-Selingue confluence and Markala Barrage further downstream [12]. After the turn at the edge of the Sahara lies the site of the Taoussa Dam. Before the confluence of Rivers Niger – Sirba is the location of the Kandadji Dam project. R. Niger enters Nigeria at the intersection of Benin-Niger-Nigeria borders, and has two large dams and a major bridge on its path – the Kainji Dam, the Jebba Dam further downstream, and the Niger Bridge just before the Niger-Delta. The R. Sokoto Rima joins the R. Niger in Nigeria first and has two dams on its path: Gussau Dam on R. Sokoto and Goronyo Dam on R. Rima. R. Kaduna joins R. Niger after the Jebba Dam and holds the large Shiroro Dam. R. Benue is the largest tributary of the R. Niger. The R. Gongola has two dams on its course – Dadin Kowa Dam and Kiri Dam [[5], [6], [11]].

Some of these dams although beneficial to human population had the river system in mind by design for example Taoussa Dam which was also designed to improve the problem of

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desertification in the Saharan proximity of the R. Niger by increasing flooding into the Saharan Lake Fagueibine system [[12]]. However, excessive evaporation in the Taoussa Dam location means that this dam not only displaces its upstream population, but denies the downstream population of a lot of flood water for agriculture; it also denies the river of a lot of discharge force midway into its journey. This is a common problem associated with dams and reservoirs, particularly those located in the Sahel climate region. Dams designed to increase the water discharge during the dry season also deprive land of recovery period after the flood, which is especially detrimental to those susceptible to erosion along the river banks.

3.2 Mining and Drilling

The land in the Niger River basin is particularly potent with natural resources and these resources are being harnessed, including Uranium mining in the upper reaches of Vallee de l'Azaouak, Iron Ore mining in Mali, Ivory Coast, and near the Niger – Benin border, Salt mining in Niger, Limestone in Mali, Coal mining at Lokoja, Lead mining in southern Nigeria, and Oil and Gas exploration in the Niger Delta region of Nigeria. Some of these mining sites are closed or have reduced activities; an example of this is coal mining in Lokoja, which had some sites closed due to an overwhelming oil exploration in Nigeria but small tributaries continuously bring water from the contaminated sites into the R. Niger. Although Vallee de l'Azaouak runs surface water mainly in the rainy season with a lot of sediments and high evaporation, a lot of its waters drain the Uranium mine site and go into the R. Niger as groundwater. After the dry season, the new rain brings heavy sediment load and "red floods" can be seen in some locations due to erosion of iron oxide rich soil. These mines are sources of pollutants which kill sensitive biota in the water [[7], [13], [14]].

3.3 Markets, festivals and traditional activities

Confluences often form good locations for markets because of their easy access to affordable transportation in different directions, particularly for live goods – a good example is Rivers Niger-Bani confluence at Mopti. River side markets put stress on the river; they often house craftsmen, such as Boat carvers and the waste products from these crafts such as wood chipping and broken equipment wash into R. Niger, piling up at the banks and eventually getting buried under settling sediments and raising the river banks. The R. Niger bank houses the largest market in Africa – the Onitsha market – at Onitsha, before the Niger Delta. Trips to markets could last from hours to days, the boats used are usually old and leak fuel into the water, and are washed at the market banks. Long haul trips have people living on the boats for days and disposing solid, animal and human waste into the water. Festivals, marriages and boat launching in Western Africa commonly involves the use of water, particularly where there is a flowing source nearby. Festivals, such as the fishing festival, harvest festivals and other sporting festivals bring numerous people into the water at the same time instantaneously decreasing the number of fishes in the water, disturbing fish spawning grounds, and often killing juvenile fishes in the water. Boat launching occasionally involves the sacrifice of animals in the river, believed to make the river accept the boat and keep it safe. Other common instream uses of the river continually stir up the water causing extended periods of high amounts of suspended sediments [[15], [16], [17], [18], [19]].

3.4 Farming, fishery and deforestation

The main occupations of people by the river side are farming and fishing. Fishing occurs along the length of the river length at depths over 0.5m. Dams such as Selingue, Talo and Kiri were created for the primary function of irrigation, and all Dams on the R. Niger were purposed to promote fishery along with their primary functions. The two deltas support rice and other crops which thrive in floods and their shallow waters also help to promote net fishing. Herdsmen also bring their livestock to the riverside to drink water as well as feed on riparian vegetation. These herdsmen often lead their cattle along the banks of the river for months, threading miles of the river banks,

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destroying vegetation and also leaving waste to be washed into the river. Practices associated with farming such as application of fertilisers and pesticides often increase the amount of certain chemicals in the water, including heavy metals such as Lead and chromium. The Inner Delta has been found to have increased levels of Lead and other heavy metals, some of which are toxic to humans and aquatic life, and come from the use of fertilizers. Also use of pesticides in cotton production has been seen to have an effect on reproduction in fish ecology. Forests are associated with acidic waters and the natural forest vegetation in the Niger Delta in Nigeria stimulates deforestation which causes severe land erosion [[20], [21]].

3.5 Flooding and Evaporation

In the Sahel Reaches of the R. Niger, the rainy season is much anticipated for the flood it brings which promotes agriculture and other pastoral livelihoods. The reach of the flood each year, serves as evidence of drought and desert encroachment but the further the reach, the more open animal and human waste it washes into the water. Although in some reaches such as the Niger Delta, year-round flooding has caused severe shortage of housing, causing entire villages to live in elevated houses on the water. Intense flooding is undesirable at inhabited areas along the river basin; it causes loss of house and property and storms and sewage drains overflow onto streets and run into the river body along with other small materials. This kind of flooding has been seen to occur along the Benue. Flooding also occurs when large amounts of rain falls over extended periods causing Dams and Weirs to give way. Evaporation is a major problem to the R. Niger because of its climate region. It is particularly a problem at places with shallow waters; evaporation is estimated to take about half of the water entering the Inner Delta, with some lose to seepage [[5], [6], [11]].

3.6 Settlement – domestic and industrial waste

River confluences also host large settlements; initially, it was predominantly for transportation and accessibility, but gradually its uses extended to provision of water upstream and disposal of wastewater downstream. In more rural areas, these settlements have compost sites which runoff into the water. Sites along the R. Gongola, R. Kaduna, and along the R. Niger in Mali have industries such as the Textile and Tannery industries, with runoffs containing high amounts of heavy metals. Pottery industries which is common among the women of Mali and Niger, often brings ash from the clay firing process. Wastewater disposal into R. Niger has been recorded at parts of Niger and Nigeria, and runoff from composting pits is the most common source of wastewater into the river at Mali [[9], [15], [18], [19]].

4. DISCUSSION

The Niger Basin Authority NBA is made up of 11 member states affected directly or indirectly by R. Niger; they deliberate on and oversee the affairs of the R. Niger and the activities on its major tributaries. In carrying out its functions, the NBA has made progress towards optimal use of the R. Niger, although natural occurrences such as great falls in the hydrological regime, uneven surface water resource distribution, including inactive regions, still lead to unequal development and cause challenges in management of the river basin [[23]]. Projects such as the Kandadji Dam – known as Kandadji regeneration of ecosystem and development of the Niger Programme – have given priority to the environment and state of the R. Niger [[24]]. Dams like Fomi which have been designed to include capacity for water discharge regulation – less water during the rainy season and more water in the dry season – will cause a decrease in the level of water in the inland delta, but will also reduce the duration of exposure of some lands to drought [[25]]. Even though new dams show increased investment in agriculture and energy, studies on the NBA proposed dams have been seen to have major impacts particularly hydrological [[26]], but the transboundary benefits of these dams

mean that undesirable impacts have to be managed across affected countries and overseen by the NBA. Predictions note areas with shallow waters exposed to desertification and parts of the inland delta drying up completely [[11]]. Dams and reservoirs displace people from their homes and as much as people need a river for sustenance, a river also needs its people because people introduce waste into the water which provides for the lower food chain and in turn supports the river's ecosystem.

Restoring the River Niger is not only a task that should be undertaken by the Niger Basin Authority NBA, but also by the people on the river bank and the local authorities. Often these people have general rules set by their unit heads as guidelines concerning location of compost pits, disposal of solid waste and parts of the river for domestic activities in order to maintain a good quality of water for drinking and fishing but the nomadic nature of some of the people, particularly in the Sahel and Fulani reaches, does not promote the continuity of a particular quality of water at a site. Less rain and decreased flooding during the rainy season is causing increased migration towards to the river bank during the dry season because water from the rainfall was not enough to last the dry season. Regulation of markets along R. Niger has become a necessity for the overall wellbeing of the river and not just the problem of market users since solid waste washes unfiltered into the river. Large markets such as Onitsha market, albeit more developed than those in Mali, do not have drainage systems adapted to the condition created by overcrowding as well as heavy rainfall; and like most markets, they have piles of solid waste around or blocking their drains, leaving poor quality surface water to flow into the river [[22]]. The NBA is not usually responsible for the standards at these markets; such responsibilities lay with the local authorities and often traders' unions. It is often the case that traders with similar products for sale form clusters to help the customers know where to go for particular items, but due to the fact that various products produce different kinds of waste, this approach keeps some parts of the market cleaner than the others.

5. CONCLUSION

The Upper Trenches of the Niger could benefit from more research to inform better decisions by the Niger Basin Authority. Most projects in this region receive funding from Worldbank, African Development Bank AFDB, humanitarian organisations and NGOs. Efforts to restore the R. Niger should come at the pipeline stage of projects. The organisations commonly involved have benchmarks to ensure minimal environmental and human impact in their projects but do not put into consideration the domino effect caused by each criterion on the other. Bearing this mind would help restore ecological connection between people and the water, and will serve as a good step towards regenerative sustainability as opposed to the current approach of using dams. Adaptation to processes of regenerative sustainability will integrate human fulfilment with environmental interests and promote socio-environmental resilience, particularly with impacts from settlements and industrial activities

Tradition rites, festivals and market activities are part of the African culture and persuading people to avoid generational activities will be futile; but taking advantage of people's consciousness of the "ways" of the river and their first-hand experience in observing the behaviour of the river in recent decades will go much further in stirring up response to environmental concerns. Though the responsibility of execution of maintenance for R. Niger will depend on cooperation from local authorities, Initiative and Funding must come from National river basin authorities, Ministries for water and agriculture, Niger Basin Authority, Non-government organisations and charities because research must be conducted into the decadal effects of year-round practices of residents in river bank communities in order to determine the best practices that ought to be adapted to each community to relieve the river. Implementation of these practices will require capital in order to less

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the burden on the residents and gain more cooperation. The foreseeable challenge with this approach is the same with most associated with adapting new practices to the culture and belief of local communities specifically those including built facilities; often, this type of environmental and humanitarian project will uncover issues like a) infrastructure built to steer clear of the river runoff is too far for residents as a result they continue using the river, b) men and women do not share common facilities and disputes also hinder neighbours from sharing hence they continue using the river; and certainly, c) the responsibility of maintenance. Factors like these continue to create challenges for organisations striving to maintain the R. Niger and demands more dynamic solutions. The Niger Basin Authority NBA stands to learn lessons from other international river basin authorities. A close example would be the R. Nile basin authority known as the Nile Basin Initiative NBI. The NBI share difficulties similar to the NBA such as unequal water resource distribution, high evaporation, pollution from tourism activities in the upper course, a very large dam in the lower course and extensive farming and fishing. Research on basin management has however progressed more in the R. Nile basin than the R. Niger basin. This is because the R. Nile has an older and more established basin authority and it runs through more countries with established education systems. Nile river basin has benefited from several research on the interaction between human activities and the environment, including the roles of the river basin management authorities as seen in [[27], [28], [29], [30]]. The Niger could learn from the Nile basin by transforming the traditional and cultural uses of the river into modern management tools [[27], [30]], and watching closely the delivery of the action plans and initiatives from the Subsidiary Action Program (SAP) and Shared Visions Program (SVP) of the NBI.

References

[1] Ward J., Kaczan, D., 2015. Challenging Hydrological Panacea: water poverty governance, accounting for spatial scale in the Niger River Basin. *Journal of Hydrology*, 519(C), 2501-2514.

[2] Djebou, D., 2015. Integrated approach to assessing streamflow and precipitation alterations under environmental change: Application in the Niger River Basin. *Journal of Hydrology: Regional Studies*, 4(B), 571 – 582.

[3] Ghile, Y., Taner, M., Brown, C., Grijsen, J., Talbi, A., 2013. Bottom-up climate risk assessment of infrastructure investment in the Niger River Basin. Climate Change. 122, 97-110.

[4] Withers, C.W., 2004. Mapping the Niger, 1798–1832: trust, testimony and 'Ocular Demonstration' in the late Enlightenment. *Imago Mundi*, 56(2), 170 – 193.

[5] FAO, 1997. Irrigation Potential in Africa a basin approach. *FAO Land and Water bulletin*, 4, 47-56.

[6] Zwarts, L., Cisse, N., Diallo, M., 2005. Hydrology of the upper Niger. *Poverty Reduction and Environmental Management program.* Available at http://www.prem-online.org/archive/11/doc/niger%20lifeline%202.pdf accessed 29 March 2016.

[7] Descroix, L., Genthon, P., Amogu, O., Rajot, J., Sighomnou, D., Vauclin, M., 2012. Change in Sahelian Rivers hydrograph: The case of recent red floods of the Niger River in the Niamey region. *Global and Planetary Change*, 98/99, 18-30.

[8] Onojake, M., Anyanwu, C., Iwuoha, G., 2012. Chemical fingerprinting and diagnostic rations of AGbada-1 Oil spill impacted sites in Niger Delta. *Eqyptian Journal of Petroleum*.

[9] LeBlanc, R., Peter, M., Richard R., 2008. Global Atlas of Excreta, Wastewater Sludge, and Biosolids Management: moving forward the sustainable and welcome uses of a global resource. *UN-HABITAT*

[10] Kousha, K., Thelwall, M., Abdoli, M., 2012. The role of online videos in research communication: A content analysis of YouTube videos cited in academic publications. *Journal of the American Society for information Science and Technology*, 63(9), 1710 – 1727.

[11] Zwarts, L., Frerotte, J-L., 2012. Water crisis in the Inner Niger Delta (Mali), Causes, consequences, solutions. *Altenburg & Wymenga ecologisch onderzoek, Feanwâlden*. Available at http://www.altwym.nl/uploads/file/490_1369389376.pdf accessed on March 29, 2016.

[12] United Nations Environmental Programme (UNEP), 2008. Ecosystem Management for improved human well-being in the Lake Faguibine system: Conflict mitigation and adaptation to climate change. *United Nations Environmental Programme* (*UNEP)*

[13] Bernert, G., 1978. Map of ground water in Niger - state of knowledge. *Ministry of mines and water - Republic of Niger*. Niamey. Available at http://infoterre.brgm.fr/rapports/79-AGE-001.pdf accessed April 27, 2016.

[14] Ezekwe, C., Odukwe, A., 1979. Coal in Nigeria. *Energy*. 5 177-182.

[15] New Atlantis, 2015. The genies of the river. *New Atlantis*. Alcobendas. Available at https://www.youtube.com/watch?v=049mNq7uSJs accessed 15 March 2016.

[16] Stop Over, 2013. A River and its people, the Niger River (Local boats) (Documentary, Discovery and History). *Stop Over*. Available at https://www.youtube.com/watch?v=SyVn8-DApTA accessed on 17 March 2016.
[17] Bemportato, D. (producer), Paolo, B. (director), Paolo, L. (photography), 2013. The way of the water – Mali. *Journeyman Pictures.* Available at https://www.youtube.com/watch?v=OCaPuZyu3-o accessed 17 March 2016.
[18] Sid Kelly, M., African Community Fishing Event – Long version – Niger River, Mali. Available at https://www.youtube.com/watch?v=3bw1q9zr-4Q accessed 17 March 2016.
[19] L'Esperance, S., (producer), Auger, E.,(sound recordist), Roberge, R., (editor) 2009. The River where we live. *Journeyman Pictures*. Available at https://www.youtube.com/watch?v=yR5d-6csORs accessed on 17 March 2016.
[20] Roger, P., 1999. Environmental impacts of wetland rice cultivation. Available at http://horizon.documentation.ird.fr/exl-doc/pleins_textes/pleins_textes_6/b_fdi_49-50/010018096.pdf. accessed March 28, 2016.
[21] Agbohessi, P., Toko, I., Ouedraogo, A., Jauniaux, T., Mandiki, S., Kestemont, P., 2014. Assessment of the health status of wild dish inhabiting a cotton basin heavily impacted by pesticide in Benin (West Africa). *Science of the Total Environment.* 506/507, 567 – 584.
[22] Aminou, S., Saidou, H., 2015. Solid Waste Management in the Town of Maradi in Niger Republic. *Scientific Research.* 6(4) Available at http://www.scirp.org/journal/PaperInformation.aspx?PaperID=55799 accessed March 29, 2016.
[23] Great Rivers Partnership, 2016. *Niger River*. Available at http://www.greatriverspartnership.org/en-us/africa/niger/pages/default.aspx accesses March 29, 2016.
[24] International Rivers, 2016. Worldbank's Kandadji Dam leaves Niger Communities High and Dry. Available at http://www.fao.org/nr/water/aquastat/data/query/index.html?lang=en accessed March 29, 2016.
[25] Worldbank, 2015. The Worldbank's engagement on the Fomi dam. *Worldbank.* Available at http://www.worldbank.org/content/dam/Worldbank/document/Africa/Guinea/fomi-fact-sheet-2015.01.pdf. accessed March 29, 2016.
[26] Diarra, S., 2011. West Africa: Niger River under Pressure *Inter Press Service News Agency*. Available at http://www.ipsnews.net/2011/10/west-africa-niger-river-under-pressure-from-dams/ accessed March 29, 2016
[27] Wantzen, K. M., Ballouche, A., Longuet, I., Bao, I., Hamady, B., Cisse, L., Chauhan, M., Girard, P., Gopal, B., Kane, A., Marchese, M., Nautiyal, P., Teixeira, P., Zalewski, M., 2016 River Culture: an eco-social approach to mitigate the biological and cultural diversity crisis in riverscapes. *Ecohydrology and Hydrobiology*. 16(1), 7-18.
[28] UNEP, 2010. Adapting to climate change in the Nile Basin. *United Nations Environmental Program*. Kenya.
[29] Awulachew, S., Smakhtin, V., Molden, D., Peden, D., 2012. *The Nile River Basin – water Agriculture, Governance and Livelihoods – Chapter one: Introduction.* International Water Management Institute. Routledge. Oxon.
[30] Khodari, N., 2003. The Nile River: Challenges to sustainable development. *Riversymposium 2003*. Australia, 7 – 12
[31] http://www.fao.org/nr/water/aquastat/main/index.stm accessed on March 21, 2016.

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Affinity of electrocoagulation process on hydrophobic/hydrophilic fraction of Baker's yeast wastewater

E. Gengec[1*], M. Kobya[2]

[1] University of Kocaeli, Department of Environmental Protection, 41275, Izmit, Kocaeli, Turkey.
[2] Gebze Technical University, Department of Environmental Engineering, 41400, Gebze, Turkey.
*Corresponding author: Email: erhan.gengec@kocaeli.edu.tr

Abstract

The baker's yeast production by fermentation cause a large quantity of wastewater which is characterized by chemical oxygen demand (COD>30.000 mg/L), biochemical oxygen demand (BOD>20.000 mg/L), total organic carbon (TOC>10.000 mg/L), strong odour, and a large amount of dark brown colour. Generally, this wastewater is treated by a combination of anaerobic and aerobic processes. In our previous study, anaerobic and anaerobic-aerobic effluents of baker's yeast wastewater were treated by electrocoagulation (EC) for the removals of color, COD and TOC in a batch EC reactor using aluminium electrodes. The maximum color, COD and TOC removal efficiencies were obtained as 88%, 48%, and 49% at 80 A/m^2, pH_i 4, and 30 min for anaerobic effluent (AE) and 86%, 49%, and 43% at 12.5 A/m^2, pH_i 5, and 30 min for anaerobic-aerobic effluent (AAE), respectively. In this study, AE, treated AE by EC (EC_{AE}), AAE, and treated AAE by EC (EC_{AAE}) were characterized by XAD-8 resin into four groups: hydrophobic bases (HoB), hydrophobic acids (HoA), hydrophobic neutral (HoN) and hydrophilic matter (HiM). All of the fractions were measured by total organic carbon analyzer and spectrophotometer (for color determination). The affinity chromatography results indicated that the HoA fractions of the wastewater were the most dominant colorful fractions, contributing to 89.12% of the AE and 88.2% of AAE. On the other hand, the HiM fractions of the wastewater were the most dominant fractions in AE and AAE according to DOC results, contributing to 60.6% and 57.6 % of DOC, respectively. The results of the EC effluents (EC_{AE} and EC_{AAE}) showed that the EC process removed the hydrophobic components more efficiently, thus color removal efficiencies were higher than DOC removal efficiencies.

Keywords: baker yeast wastewater; affinity chromatography; electrocoagulation; hydrophobic/ hydrophilic

1. INTRODUCTION

It is not known that yeast have used to bake bread from Ancient Egypt. Since the end of the nineteenth century, baker's yeast has been produced by companies that specialize in its production. Nowadays, the companies produce hundreds of thousands of metric tons of yeast each year in industrial plants. The baker's yeast production process involve four basic steps (I) molasses and other raw material preparation, (II) culture or seed yeast preparation, (III) fermentation and harvesting, (IV) filtration and packaging. During the production of baker's yeast by fermentation, a large quantity of wastewater (BYW) were produced which have extremely high chemical oxygen demand (COD>30.000 mg/L), biochemical oxygen demand (BOD>20.000 mg/L), total organic carbon (TOC>10.000 mg/L), strong odor, and a large amount of dark brown color. The dark brown color in these effluents is originated by the pigment called melanoidins which are resistance to biodegradation [1,2]. The dark brown color of BYW interferes with the absorption of sunlight which reduces the natural process of photochemical reactions for self-purification of the surface waters.

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Up till now, various treatment methods such as biological process (anaerobic, aerobic), physico-chemical treatment (adsorption, membrane process, reverse osmosis, coagulation/ flocculation) and oxidation processes (ozone, Fenton) have been attempted for the treatment of BYW. Biological treatment of BYW, which are most commonly used methods, involves combinations of anaerobic digestion and aerobic systems that successfully reduce BOD to acceptable limits, but does not deal effectively with either the dark color or the associated COD that remains and limits the reuse/recycling of the process water [3–6] (Table 1).

In our previous study, anaerobic and anaerobic-aerobic effluents of baker's yeast wastewater were treated by electrocoagulation (EC) for the removals of color, COD and TOC in a batch EC reactor using aluminium electrodes. The maximum color, COD and TOC removal efficiencies were obtained as 88%, 48%, and 49% at 80 A/m^2, pH_i 4, and 30 min for anaerobic effluent (AE) and 86%, 49%, and 43% at 12.5 A/m^2,pH_i 5, and 30 min for anaerobic-aerobic effluent (AAE), respectively [4].

Although our previous studies have been conducted on the decolorization of the BYW by EC[4], there are no studies related to understand the effect of the hydrophobic/hydrophilic fractions in BYW to the color and dissolved organic carbon (DOC) and the affinity of EC removal mechanism on hydrophobic/hydrophilic fractions. Thus, the ratios of hydrophobic/hydrophilic fractions in BYW were investigated in this study to evaluate color and DOC removal mechanism of EC processes.

2. MATERIALS AND METHODS

2.1 Wastewater

BYW were obtained from a Baker's yeast-manufacturing factory in Kocaeli, Turkey. It had a full scale two-stage anaerobic and aerobic biological treatment plant. The wastewater samples collected from anaerobic effluent (AE), and anaerobic-aerobic effluents (AAE) were characterized (Table 1). As seen in Table 1, the anaerobic and anaerobic-aerobic stages from BYW were effective in removing COD (92.2% and 98.0%) except for color (23.6% and 73.6%).

Table 1. Characterizations of biologically treated baker's yeast wastewater

Parameters	Anaerobic influent	Anaerobic Effluent (AE)	Anaerobic-aerobic Effluent (AAE)
pH	5.6	7.2	7.7
Temperature (^{0}C)	24	30	25
Conductivity (mS/cm)	17.24	17.42	7.46
TS (g/L)	22.2	15.2	5.1
TVS (g/L)	10.3	4.5	0.72
TSS (g/L)	1.01	5.08	0.04
Alkalinity (mg/L)	750	4130	1050
COD (mg/L)	27920	2160	544
TOC (mg/L)	6090	919	184
Color (Abs_{475nm}/cm)	2.50	1.91	0.66
Absorbance (Abs_{254nm}/cm)	2.92	2.78	2.72
TKN (mg/L)	648	421	39
NH_3-N (mg/L)	560	297	19
TP (mg/L)	17.5	12.8	2.05
PO_4-P (mg/L)	9.75	9.72	1.79

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2.2. Experimental set-up and procedure

The EC treatment was carried out in a batch electrolytic reactor made from Plexiglas material with dimensions of 100 mm × 100 mm × 130 mm. Four aluminum electrodes in the reactor were used as cathodes and anodes with effective dimensions of 80 mm×50 mm×3 mm. Total effective areas of electrodes were 240 cm^2. The electrodes were situated 5 mm apart from each other and connected to monopolar parallel connection mode.

Before each run, the electrodes were dipped into solutions of HCl (35%) and hexamethylenetetramine (2.8%) to remove the oxide and/or passivation layers from the electrodes[4]. The electrodes were placed in the reactor and solutions were mixed at 300 rpm in the EC reactor. In each run, 0.8 L sample was placed into the EC reactor. The current density (CD) was adjusted by a digital DC power supply (TDK-Lambda Genesys model; 50 V-30A) operated at galvanostatic mode and the experiment was started. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces and dried. All experiments were performed at 25 ^oC.

2.3. Analytical method

The samples were filtered using a 0.45 μm Whatman glass microfiber filter for COD and TOC. Total COD and TOC were measured according to standard methods [7]. COD was measured by closed reflux titrimetric method and TOC levels were determined through combustion of the samples at 680 °C using a non-dispersive IR source (Tekmar Dohrmann Apollo 9000). Initial pH (pHi) of sample was adjusted with H_2SO_4 or NaOH and measured by pH meter (WTW Inolab pH 720). Color contents were measured using a UV–vis spectrophotometer at 475 nm (Perkin-Elmer 550 SE) [8].

2.4. Chromatographic separation

There is a growing interest on the part of researchers to determine the affinity of natural organic compounds in water/wastewater and it is clear that affinity of compounds affect the removal mechanism in different treatment systems. In recent years, it has been found that high recoveries of organic compounds from water/wastewater are possible with macroreticular Amberlite XAD resins. These resins are nonionic, macroporous copolymers which possess large surface areas. There has been much study of the use of XAD resins for isolation, concentration, and chromatographic separation of many classes of compounds [10–14]. Many of researcher were interested with development and modification of resins adsorption [10,15]. Thus, this methods have extensively used to separation of natural organic compounds [12].

In this study, fractions of BYW were realized by sorption on the XAD-8 resin at the controlled polarity to quantitatively into hydrophobic-base (HoB), -acid (HoA), and –neutral (HoN) fractions and hydrophilic (HiM) fractions. This procedure based upon adsorption on ion-exchange resin adsorbents. Amberlite XAD-8 polymeric resins is a non-ionic, hydrophobic, and cross-linked polymer [9–11]. The resins were cleaned and conditioned as described by Leenheer et al., (1981) [10]. First, resins were extracted by acetone and hexane by sequential 24 hours by Soxhlet extractor for removing organic substances. Then, the resins were rinsed with 0.1 N NaOH, 0.1 N H_3PO_4, and distilled water. Cleaned XAD-8 resin was stored in methanol. Then, the modified procedure, which was described by Wei et al., (2008) [12] and Vojvodic et al., (1994) [13], was used for fractionation of organic matter into hydrophobic and hydrophilic fractions by sorption on the XAD-8 resin (Fig 1).

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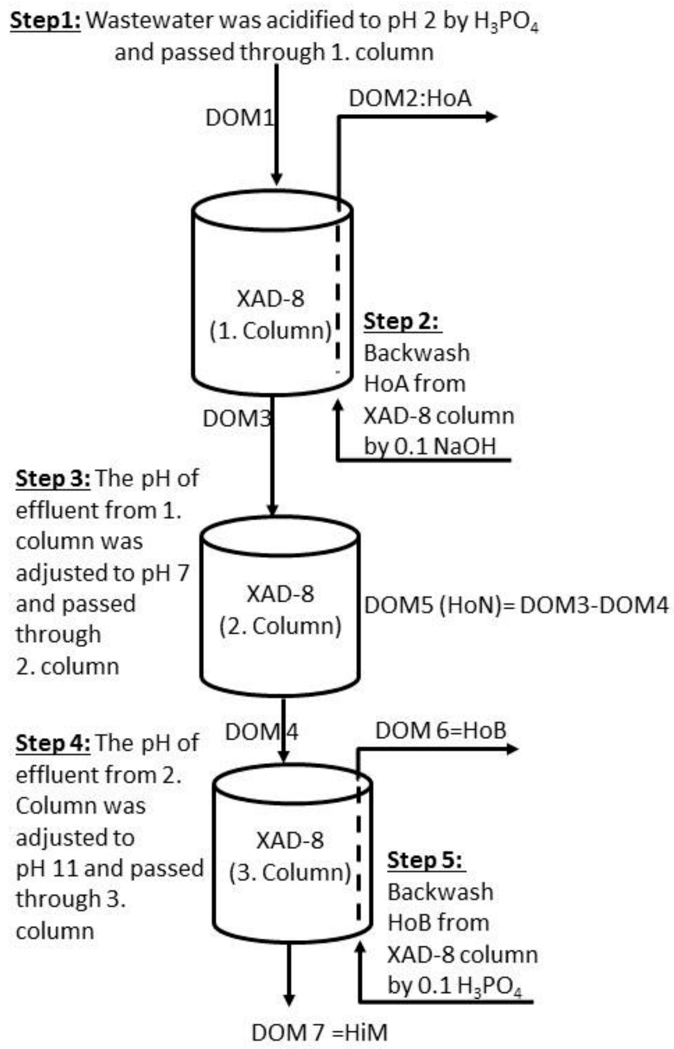


Figure 1. The fractionation procedure of BYW by XAD-8

The fractionation procedure steps of BYW by XAD-8 were as following: (1) the pH of filtered sample was adjusted to 2 by H_3PO_4 and then passed through XAD-8 resin (2) HoA was obtained by backwashing the XAD-8 resin immediately with 10 bed-volumes of 0.1 mol/L NaOH (3) the pH of effluent from 1. column was adjusted to 7 and passed through 2. column (HoN was adsorbed in 2. column and HoN was calculated by the difference from effluent of 1. and 2. column) (4) the pH of effluent from 2. column was adjusted to 11 and passed through 3. column (effluent of 3. column was HiM) (5) the adsorbed fraction in 3. column was backwashed to obtain HoB by 0.1 mol/L H_3PO_4. Finally DOC and color (AU_{475}) of all fractions were measured.

3. RESULTS AND DISCUSSION

In our previous study, anaerobic and anaerobic-aerobic effluents of BYW were treated by electrocoagulation for the removals of color, COD and TOC in a batch EC reactor using aluminium electrodes. The optimum color, COD and TOC removal efficiencies were obtained as 88%, 48% and 49% at 80 A/m^2, pH_i 4 and 30 min for anaerobic effluent (AE) and 86%, 49% and 43% at 12.5 A/m^2,pH_i 5 and 30 min for anaerobic-aerobic effluent (AAE), respectively. In this study, the

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contribution of the hydrophilic and hydrophobic organic compounds in BYW to color and DOC of the wastewater were measured by adsorption chromatograph for determination of the electro-coagulation affinity on compounds.

Adsorption chromatography was applied to raw (AE and AAE) and treated wastewater by electrocoagulation (EC_{AE} and EC_{AAE}). Then, DOC, color (at 475 nm) and the aromatic character of compounds (at 254 nm) in BYW were determined as seen in Table 2-4 and Fig. 2.

Table 2. The DOC results of fractioned AE, AAE, EC_{AE} and EC_{AAE} wastewater by XAD-8 resins

	DOC							
	AE		AAE		EC_{AE}		EC_{AAE}	
	mg/L	Ratio (%)	mg/L	Ratio (%)	mg/L	Ratio (%)	mg/L	Ratio (%)
Measured Total	935.5	100.0	142.3	100.0	591.5	100.0	53.8	100.0
HoA	402.9	43.1	66.7	46.8	195.6	33.1	18.4	34.2
HoN	27.6	3.0	1.7	1.2	-19.9	-3.4	-0.6	-1.1
HoB	-62.1	-6.6	-8.0	-5.6	-4.2	-0.7	-2.6	-4.8
HiM	567.1	60.6	82.0	57.6	420.0	71.0	38.6	71.8
Calculated Total	935.5	100.0	142.4	100.0	591.5	100.0	53.8	100.1

Table 3. The absorbance results at 254 of fractioned AE, AAE, EC_{AE} and EC_{AAE} wastewater by XAD-8 resins

	254 nm							
	AE		AAE		EC_{AE}		EC_{AAE}	
	AU	Ratio (%)	AU	Ratio (%)	AU	Ratio (%)	AU	Ratio (%)
Measured Total	0.204	100.0	0.060	100.0	0.064	100.0	0.054	100.0
HoA	0.166	71.6	0.033	50.8	0.006	6.0	0.011	12.9
HoN	0.002	0.9	-0.003	-4.3	0.001	1.0	0.001	1.2
HoB	0.003	1.3	-0.002	-3.4	0.029	28.9	0.025	28.7
HiM	0.061	26.3	0.037	56.9	0.064	64.1	0.049	57.2
Calculated Total	0.232	100.0	0.065	100.0	0.100	100.0	0.086	100.0

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Table 4. The color results of fractioned AE, AAE, EC_{AE} and EC_{AAE} wastewater by XAD-8 resins

475 nm								
	AE		AAE		EC_{AE}		EC_{AAE}	
	AU	Ratio (%)	AU	Ratio (%)	AU	Ratio (%)	AU	Ratio (%)
Measured Total	1.491	100.0	0.381	100.0	0.150	100.0	0.044	100.0
HoA	1.328	89.1	0.338	88.2	0.134	87.5	0.036	78.9
HoN	0.118	7.9	0.031	8.1	0.000	0.0	0.000	0.0
HoB	0.002	0.1	0.001	0.4	0.001	0.8	0.001	1.3
HiM	0.043	2.9	0.013	3.4	0.018	11.7	0.009	19.7
Calculated Total	1.491	100.0	0.383	100.0	0.153	100.0	0.046	100.0

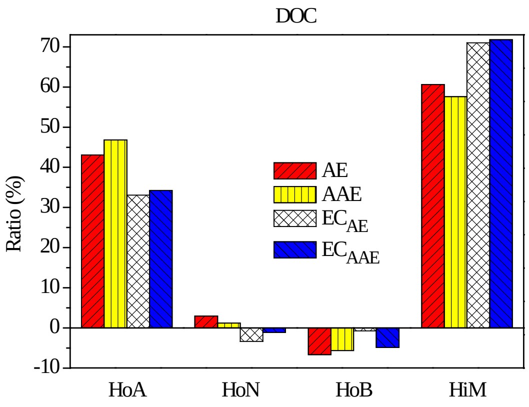
As seen in Table 2, the HiM fractions of wastewater had a large amount of contribution to DOC and contribution ratio of the HiM fractions to AE, AAE, EC_{AE} and EC_{AaE} were measured as 60.6%, 57.6%, 71.0 and 71.8%, respectively. On the other hand, the low or negative values of HoN and HoB were very attractive. Two possible reasons may cause these the negative values. First, the dilution of wastewater during adjustment of pH decreased the wastewater's DOC. Second, the precipitation of the some organic compounds in BYW at higher pH were realized as reported before[3]. Probably, XAD resins acted as a filtrate for these precipitated organic compounds. In addition, similar negative results, obtained during the separation of organic compounds by XAD resin, were reported in literature [9].

As seen in Table 3-4, the highest contribution for color was originated by HoA and the color contribution ratio of the HoA fractions to AE, AAE, EC_{AE} and EC_{AaE} were measured as 89.1%, 88.2%, 87.5% and 78.9%. The lower contribution results of other fractions (HoN, HoB and HiM) to color showed that the color of wastewater was originated by HoA compounds. These results was well agreement with literature [9].

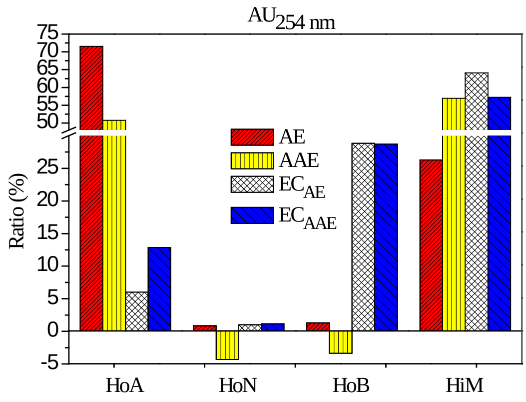
According to DOC results, after anaerobic treatment the ratio of HoA increased and the ratios of HoN and HiM decreased. The changing in HoB was not significant. On the other hand, after EC treatment the ratios of HoA and HoN decreased and the ratios of HoB and HiM increased. The similar results were obtained in color measurement. According to color and DOC results, the HoB and HoN fractions had not an important contribution to color and organic contents.

As seen in Fig.2, HoA fractions of AE were changed from 402.9 mg/L to 195.6 mg/L during EC and removal realized as about %51. Although, HiM fractions of AE were changed from 576.1 mg/L to 420.0 mg/L during EC and removal of DOC realized as only about %25.9. Similar trends were obtained in treatment of AAE by EC. HoA fractions of AAE were changed from 66.7 mg/L to 18.4 mg/L during EC and removal realized as about %72.4. HiM fractions of AAE were changed from 82.0 mg/L to 38.6 mg/L during EC and removal of DOC realized as only about %53.0. These results showed that the preferential removal of HoA fractions was realized by EC.

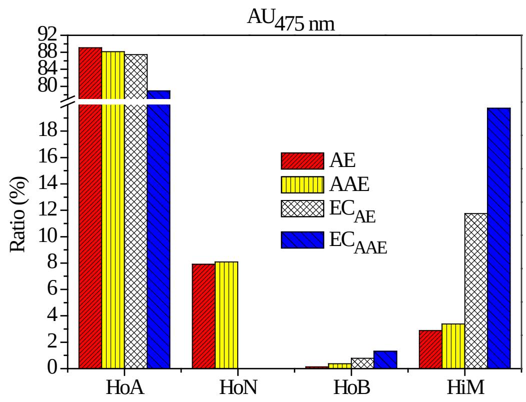
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(a)



(b)



(c)

Figure 2. The results of fractioned AE, AAE, TAE and TAAE wastewater by XAD-8 resins

4. CONCLUSIONS

In this study, anaerobic and anaerobic-aerobic effluents of baker's yeast wastewater were treated by electrocoagulation (EC) for the removals of colour, and TOC in a batch EC reactor using aluminium electrodes. The maximum color, COD and TOC removal efficiencies were obtained as 88%, 48% and 49% at 80 A/m^2, pH_i 4, and 30 min for anaerobic effluent (AE) and 86%, 49%, and 43% at 12.5 A/m^2,pH_i 5, and 30 min for anaerobic-aerobic effluent (AAE), respectively. In addition to, AE, treated AE by EC (EC_{AE}), AAE, and treated AAE by EC (EC_{AAE}) were characterized by XAD-8 resin into four groups: hydrophobic bases (HoB), hydrophobic acids (HoA), hydrophobic neutral (HoN) and hydrophilic matter (HiM). The affinity chromatography results indicated that HOA were the most dominant colourful fractions, contributing to 89.12% of the AE and 88.2% of AAE. On the other hand, HiM were the most dominant fractions in AE and AAE according to DOC results, contributing to 60.6% and 57.6 % of DOC, respectively. The results of the EC effluents (EC_{AE} and EC_{AAE}) showed that the EC process removed the hydrophobic components more efficiently.

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References

1. Pant, D. & Adholeya, A. Biological approaches for treatment of distillery wastewater: a review. *Bioresour. Technol.* **98,** 2321–34 (2007).
2. Agarwal, R., Lata, S., Gupta, M. & Singh, P. Removal of melanoidin present in distillery effluent as a major colorant: A review. *J. Environ. Biol.* **31,** 521–528 (2010).
3. Kobya, M. & Gengec, E. Decolourization of melanoidins by a electrocoagulation process using aluminium electrodes. *Environ. Technol.* 1–10 (2012). doi:10.1080/09593330.2012.671371
4. Gengec, E., Kobya, M., Demirbas, E., Akyol, A. & Oktor, K. Optimization of baker's yeast wastewater using response surface methodology by electrocoagulation. *Desalination* **286,** 200–209 (2012).
5. Gengec, E. & Kobya, M. Treatment of Baker's Yeast Wastewater by Electrocoagulation and Evaluation of Molecular Weight Distribution with HPSEC. *Sep. Sci. Technol.* **48,** 2880 – 2889 (2013).
6. Gengec, E., Kobya, M., Demirbas, E., Akyol, a. & Oktor, K. Electrochemical treatment of Baker's yeast wastewater containing melanoidin: Optimization through response surface methodology. *Water Sci. Technol.* **65,** 2183–2190 (2012).
7. APHA. *Standard Methods for the Examination of Water and Wastewater*. (American Public Health Association, 1998).
8. Krishna Prasad, R. & Srivastava, S. N. Electrochemical degradation of distillery spent wash using catalytic anode: Factorial design of experiments. *Chem. Eng. J.* **146,** 22–29 (2009).
9. I, X. Z., Zuoi, C. M. & Engineering, C. The main components of color and dissolved organic matter from yeast industry effluent DOC Analytical conditions . DOC measurements Characterisation of HOA by SPE-GCIM DOMfractionation A . DOM-fraction distribution of raw effluent (DOM) o. 833–836
10. Cited, L. We acknowledge Elgin Perry for the statistical analysis of these data, Jeanie Arciprete for typing the manuscript, and Mike Jepson for his technical assistance. Special consideration is extended to Dr. Randy Roig for his technical review. *Science (80-.).* (1981).
11. Aiken, G. & Thurman, E. Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution. *Anal. Chem.* **51,** 1799–1803 (1979).
12. Wei, Q. S. *et al.* Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study. *J. Hazard. Mater.* **150,** 257–264 (2008).
13. Vojvodic, V., Cosovic, B. & Miric, V. Fractionation of surface active substances on the XAD-8 resin. Part I. Mixtures of model substances. *Anal. Chim. Acta* **295,** 73–83 (1994).
14. Matilainen, A. *et al.* An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere* **83,** 1431–1442 (2011).
15. Thurman R.L., E. M. and M. Preparative isolation of aquatic humic substances: *1981 Am. Chem. Soc.* **15,** 463–466 (1981).

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Humic acid removal from aqueous solution by fixed-bed electrocoagulation reactor using Al ball anodes

F. Ulu[1], E. Gengec[2], M. Kobya[1]

[1] Department of Environmental Engineering, Gebze Technical University, 41400, Gebze, Turkey.
[2] Department of Environmental Protection, Kocaeli University, Arslanbey, Kocaeli, Turkey.
* Corresponding author: Email: erhan.gengec@kocaeli.edu.tr

Abstract

The natural organic matter (NOM) present in water bodies is a complex mixture of organic substances such as humic and fulvic acids, proteins, lipids, hydrocarbons and amino-acids. The major fraction of the NOM occurs by degradation of plants and animals residual in terrestrial areas and aquatic systems. The NOM is a direct problem in drinking water due to colour and taste. Indirectly, NOM is a problem because it reacts with the most commonly used disinfectants, chlorine, to form disinfection by-products some of which have been associated with an increased risk of cancer. NOM can be define according to its biophysico-chemical functions and properties, as humic (humic and fulvic acid) and non-humic substances (hydrophilic acids, carboxylic acids, amino acids, carbohydrates, hydrocarbons). Humic substances (HSs) basically humic acids (HAs) that are comprised of highly functionalized carbon rich polydisperse polyelectrolytes are the major fraction of naturally occurring organic matters. Thus, the removal of HAs is an essential process. This investigation was focused on develop of an innovative reactor and electrode configuration for the removal of humic acid (HA). The fixed-bed electrocoagulation reactor comprised of aluminium ball anode electrodes that placed in a cylindrical reactor. DOC and UV_{254} were taken in account for reveal the removal efficiency of HA. The effect of initial pH (pH_i), current density (j, mA/cm^2), operating time (min, t), and initial humic acid concentration (C_o, mg/L) were investigated. The result showed that the maximum DOC and UV_{254nm} removal efficiencies were obtained at 4 of pH , 6 mA/cm^2 of current density and 30 mg/L of initial HA concentration as 90.76 and 95.66 %, respectively.

Keywords: humic acid; electrocoagulation; fix-bed; Al electrode

1. Introduction

The natural organic matter (NOM) present in soil, sediment, and water bodies is a complex mixture of organic substances. The major fraction of the natural organic matter (NOM) occurs by degradation of plants and animals residual in terrestrial areas and aquatic systems. The environment in which NOM is formed plays a critical role in determining the specific properties of any given sample of NOM. Humic substances as the dominate fraction of aquatic NOM constitute 40-60 percent of dissolved organic matter (DOM) in natural fresh surface waters [1]. NOM can be define as humic (humic and fulvic acid) and non-humic substances (hydrophilic acids, carboxylic acids, amino acids, carbohydrates, hydrocarbons.). NOMs constitute a severe subject in natural and engineering systems. NOMs are effective in transporting of the metals and organic pollutants. The NOM is a direct problem in drinking water due to colour and taste. Also, NOM is a problem because it reacts with the most commonly used disinfectants, chlorine, to form disinfection by-products (DBP's) some of which are mutagenic and carcinogenic during the chlorination process in water treatment systems [2]. Consequently, removal of HA from surface water or wastewater is major and considered of great health and environmental concern. Apart from conventional

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treatment process, activated carbon filtration, ion exchange, membrane filtration techniques [3,4], and advanced oxidation processes [5] are placed in literature for removal of NOM from water. But many of the above treating methods have some problems such as annual high operation costs, process control, flux decline and the membrane fouling in membrane processes.

Recently, electrocoagulation (EC) has been suggested to be a promising alternative to chemical coagulation for removing various pollutants from water and wastewaters [6, 7]. This method has a lot of advantages when compared to conventional and advanced water treatment methods such as simple equipment, easy to operate, low maintenance cost, short operating times, not consumed of alkalinity; not needed of pH adjustment, cost-effective, reduction or absence of adding chemicals, rapid sedimentation of the electrogenerated flocs and lower quantities of produced sludge and environmental compatibility [8, 9]. EC treatment is a complicated process involving many chemical and physical phenomena. EC process depends on a current that is applied from an external power pass through the electrodes in an electrochemical reactor. Mainly the metal ions (Al^{3+}, Fe^{2+} and Fe^{3+}), are in situ generated by electrolytic oxidation of the sacrificial iron or aluminium electrode materials. At the same time, the reduction of water, which occurs on the cathode, participates to the elimination process owing to the production of hydroxide ions and hydrogen gas. Two major interaction mechanisms are being considered in recent years; precipitation and adsorption, each being proposed for a separate pH range.

EC process has proved to be efficient with regard to the removal of aquatic humus and including high NOM concentration water [10, 11]. The effective removal of HSs from aqueous solution has been proved with EC studies but the significant gaps present looking at literature about electrode shape, reactor design, operation condition.

The design of the EC process influences its operation and efficiency. From the literature, the most common approach involves plate Al or Fe electrodes in EC reactors. The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced. However, changing and maintenance of these electrodes used in the EC reactors are time consuming and not practical. Therefore, new fixed bed EC reactors used of Fe or Al ball anodes have specifications of compactness, easy to use, accommodating of more anode electrodes with higher surface areas and providing better removal efficiency for the HSs removal from water.

This investigation was focused on develop of an innovative reactor and electrode configuration for the removal of NOM. The fixed-bed electrocoagulation reactor comprised of aluminium ball anode electrodes that placed in a cylindrical reactor. The optimum conditions were determined by TOC and UV_{254}/VIS_{436} measurements.

2. MATERIALS AND METHODS

2.1. Material

In this study, synthetic waste water was prepared using tap water with adding different humic acid concentrations. Humic acid was supplied from Sigma-Aldrich. 1000 ppm stock humic acid solution was prepared in dissolving 0.1 N NaOH. The initial concentrations of synthetic waste water were prepared as 50, 30, and 10 ppm by dilution the stock humic acid solution and the initial DOC value of solutions were 16.92 mg/L, 10.28 mg/L and 5.61 mg/L, respectively. The UV_{254} was 1.433 cm^{-1}, 0.863 cm^{-1}, and 0.291 cm^{-1} of raw synthetic solution (no pH adjustment) for 50 ppm, 30 ppm, and 10 ppm, respectively. The pH value of the synthetic solution was adjusted before the experiments by the addition of H_2SO_4 ve NaOH. All experiments were conducted at room temperature (20±1 ^oC). The characterization of tap water that used in this study was given Table 1.

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Table 1. The characterization of tap water

Parameters	Value
pH	7.6
Conductivity (mS/cm)	0.85
Dissolved Oxygen (mg O_2/L)	6.2
Chloride (mg/L)	0.35
Sulphate (mg/L)	18
Alkalinity (mg/L $CaCO_3$)	85
Total Hardness (mg/L $CaCO_3$)	120

2.2. Experimental set-up and procedure

In this study, the removal of HS was conducted in batch mode by EC process. The structure of EC reactor was shown in Figure 1. Al ball electrodes that were used as anode were put into a cylindered like a nett for prevent connection with cathode. 1000 mL synthetic HA solution was put into cylindrical fibreglass batch reactor (Figure 1). The air supply was done from bottom for mix of solution in the reactor via air compression. Air flow rate was measured by a gas flowmeter. The samples that were taken from reactor certain interval were filtered through 0.45 µm pore size membrane before UV/VIS, NPOC (Non-Purgable Organic Carbon) analysis. Before the experiments, electrodes washed with 0.5 N H_2SO_4 solution and rinsed with deionized water, then dried in the oven and put in a desiccators to cool down. After each experiment, the same process was applied.

Cylindrical titanium electrode that has 72 mm diameter was used as cathode in EC reactor. Al ball electrodes were used as cathode in the range of 5-10 mm diameter. A titanium rod was placed in the middle of anode material (Figure 1). These (anode) electrodes were put into an all porous surface cylindrical vessel (almost 3 L) that is made of polymeric/plastic like a nett for prevent connection with cathode. Current and voltage at anode and cathode were checked (observed) with a DC power supply. Experiments were conducted at constant current.

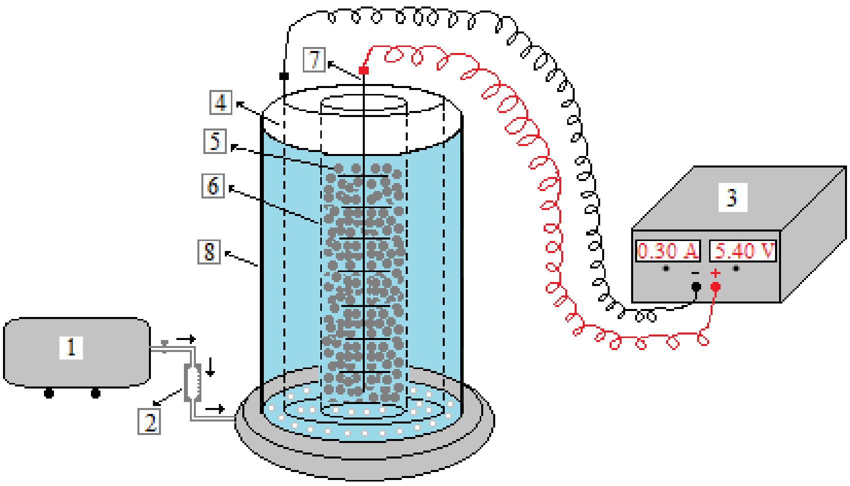


Figure 1. A schematic diagram of the air fed EC reactor (1. Air compressor, 2. Air flow meter, 3. DC power supply, 4. Cylindrical shaped titanium (Ti) cathode, 5. Al ball anodes,6. Polymeric/plastic nett, 7. Titanium rod, 8. EC reactor).

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2.3. Analytical methods

The turbidity, dissolved oxygen, conductivity and pH parameter were measured by Mettler Toledo device. Absorbance readings were carried out by Perkin Elmer Lambda 35 UV/VIS Spectro-photometer. DOC concentration samples were determined by the high combustion Schimadzu TOC-L analyzer equipped using NPOC method with auto sampler.

3. RESULTS AND DISCUSSION

3.1. Effect of initial pH on HS removal

In EC process, the pH is one of the most important parameters due to the effect on both metal hydroxide species and pollutant parameters in wastewater. In experiments, initial pH (pH_i) values were arranged to 4, 6, and 8. The operating time means that electrolysis time of EC process and it was 25 min.

As it is seen in Figure 2.a), the highest treatment efficiency for HA solution was 90.8% with DOC treated 0.95 mg/L at pH_i 4 end of the process at constant current density of 6 mA/cm^2 and 30 ppm of initial concentration of HA. At 6 and 8 of pH_i, DOC removal efficiency was reduced 85.6% and 55.8% with effluent DOC concentration of 1.48 mg/L and 4.53 mg/L, respectively, at the end of the process. The reactive stage continued until 15 min electrolysis time for pH_i 4. Stabilizing stage was observed after this time. The reactive stage continued until almost the end of the process for pH_i 6 and 8. Obviously, the lower pH values led to faster removal and better efficiency in DOC.

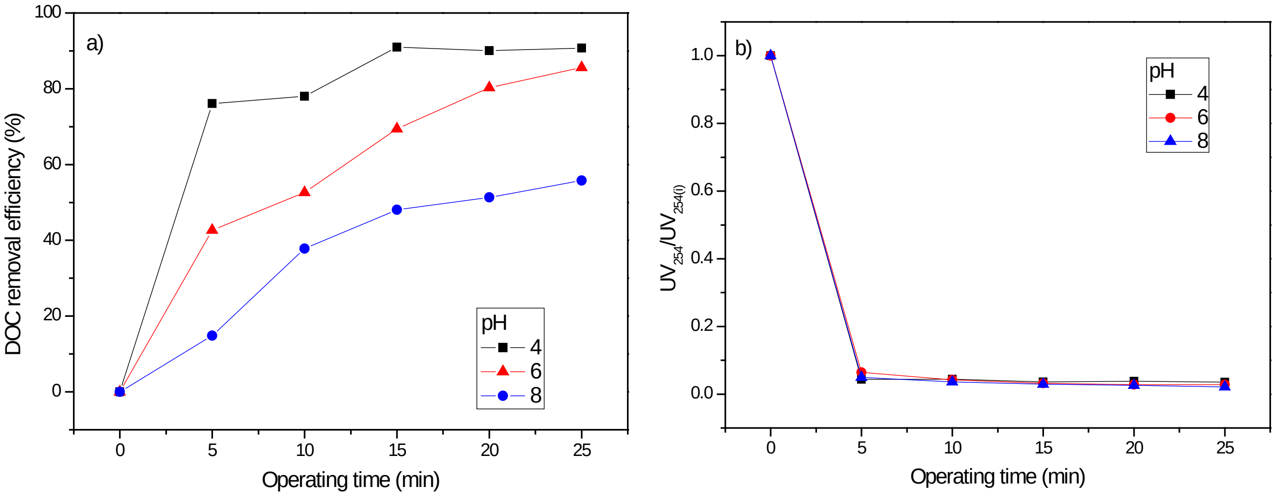


Figure 2. The effect of pH on a) DOC removal efficiency b) UV_{254} reduction during EC process pH (j=6, initial HA concentration=30 ppm).

Aluminum species has a more positive charge at low pH when they were formed in acidic initial pH due to lack of hydrolysis. It can be concluded that negative charge centers on the macromolecule of functional groups of organic substance to which Al cations are strongly attracted and destabilization of colloid occur. Figure 2.b) shows UV_{254} removal efficiency was 95.7% at 4 of pH_i.

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3.2. Effect of current density on HS removal

The amount of dissolving metal from anode electrodes increase with enhancement current density and the higher removal efficiency of pollutant can obtain. But, a limited current density value is recommended in order to avoid some negative effect on process such as higher energy consume, breakage of occurred flocs, the heating of solution.

Figure 3, shows the effect of different current densities on HS removal with respect to DOC and UV_{254} at 6 of pH_i. The studied current densities were 2 mA/cm^2, 6 mA/cm^2 and 10 mA/cm^2. Higher current density led to more HS removal efficiency. At 25 min, 85.6% ($DOC_{treated}$ 1.48 mg/L) of humic acid removal can be achieved with a current density of 6 mA/cm^2, but 65.9% ($DOC_{treated}$ 3.50 mg/L) of removal was obtained when the current density was reduced to 2 mA/cm^2 with Al electrodes at pH_i 6, as it is seen in Figure 3.a). But, at 10 mA/cm^2 of current density of, DOC reduction was 83.3%. It can be concluded that the DOC removal efficiency would not increase after a certain current density (optimum current density). The maximum DOC removal efficiency was obtained at 6 mA/cm^2 of current density and UV_{254} reduction was 97.2% (Figure 3.b).

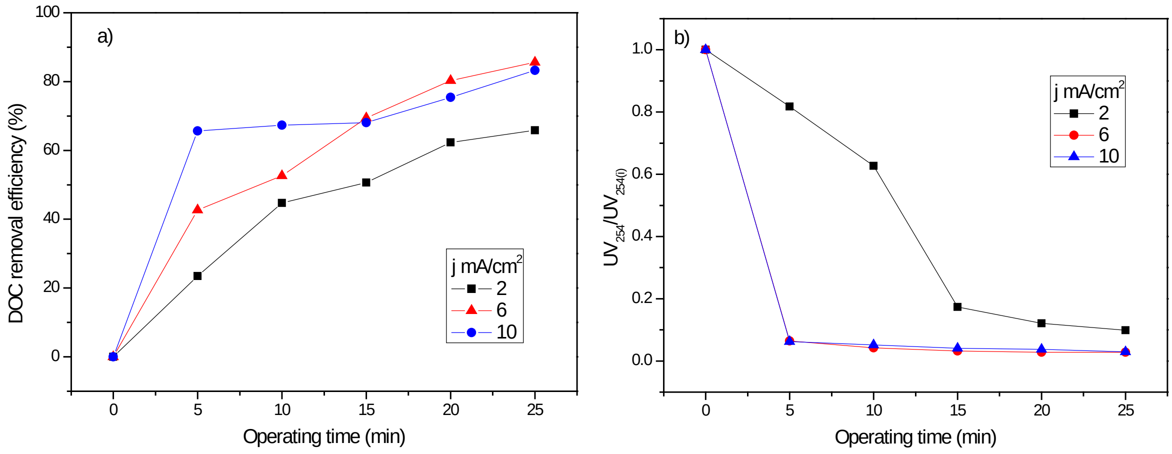


Figure 3. The effect of current density on a) DOC removal efficiency b) UV_{254} reduction during EC process (pH_i=6, initial HA concentration=30 ppm)

3.3. Effect of initial concentration on HS removal

As it is seen in Figure 4, the effect of initial concentration of HA solution was investigated at optimum current density and pH_i. HA solution including the lowest concentration was the most resistant to EC treatment with DOC reduction of 55.9% ($DOC_{treated}$ 2.48 mg/L). When the concentration of solution was increased, the removal efficiency was increased as 85.6% ($DOC_{treated}$ 1.4 mg/L), 90.2% ($DOC_{treated}$ 1.66 mg/L) for 30 ppm and 50 ppm, respectively, at the end of the electrolysis time. At highest concentration, removal rate was fast until 5 min. After this electrolysis time the removal rate was increased. As it is seen in Figure 4.a), reactive phase could continue after 25 min at 10 ppm, and 30 ppm. At lower concentration the in situ produced Al coagulants didn't react with organic matter immediately. The more electrolysis time requires in order to increasing removal efficiency.

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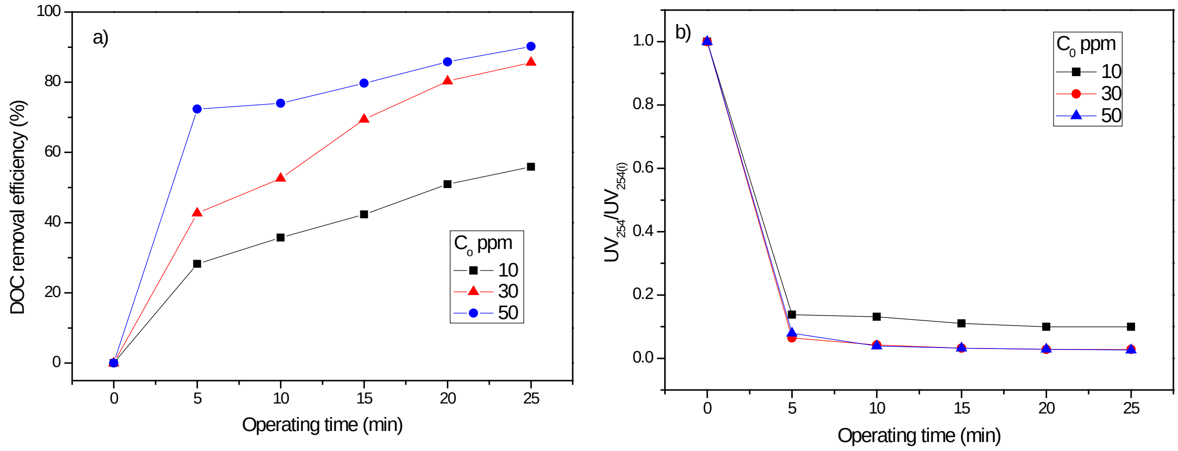


Figure 4. The effect of initial HA concentration on a) DOC removal efficiency b) UV_{254} reduction during EC process (j=6 mA/cm^2, pH=6).

4. CONCLUSIONS

This study represents the treatability of humic matter by EC process using Al anode electrodes. Sigma HA used as natural organic matter in drinking water supplies. The maximum removal efficiency was obtained 90.76% with DOCtreated 0.95 mg/L at pH_i 4 and 6 mA/cm^2 of current density. UV254 reduction was 95.7% with 0.037 cm^{-1} at optimum conditions. It can be concluded that initial pH have major effect on the removal of DOC and UV_{254}. The current density should be optimized. The removal performance of organic matter including different concentration depends on the effective electrolysis time. The operating time and NOM concentration were other two parameters that should be considered with respect to NOM removal during EC process.

References

[1] Rebhun M., Lurie M., (1993), "Control of organic matter by coagulation and floc separation", Atmosphere, 638, 02.
[2] Selcuk S., Meric S., Nikolaou A.D., Bekbolet M., A comparative study on the control of disinfection by-products (DBPs) and toxicity in drinking water, Desalination and Water Treatment, 26 (2011) 165-171.
[3] Gray S.R., Ritchie C.B., Tran T., Bolto B.A., Effect of NOM characteristics and membrane type on microfi ltration performance, Water Research, 41 (2007) 3833-3841.
[4] Kabsch-Korbutowicz M., Effect of Al coagulant type on natural organic matter removal efficiency in coagulation/ultrafiltration process, Desalination, 185 (2005) 327-333.
[5] Bekbolet M., Suphandag A.S., Uyguner C.S., An investigation of the photocatalytic efficiencies of TiO_2 powders on the decolorisation of humic acids, J. Photochem. Photobiol. A: Chem. 148 (2002) 121–128.
[6] Kuokkanen V., Kuokkanen T., Ramo J., Lassi U., Recent applications of electrocoagulation in treatment of water and wastewater-A review, Green and Sustainable Chemistry, 3 (2013) 89-121.
[7] Kabdasli I., Arslan-Alaton I., Olmez-Hanci T., Tunay O., Electrocoagulation applications for industrial wastewaters: a critical review, Environmental Technology Reviews, 1 (2012) 2-45.
[8] De Mello Ferreira A., Marchesiello M., Thivel P.X., Removal of copper, zinc and nickel present in natural water containing Ca^{2+} and HCO_3 ions by electrocoagulation, Separation and Purification Technology, 107 (2013) 109-117.
[9] Kobya M., Hiz H., Senturk E., Aydiner C., Demirbas E., Treatment of potato chips manufacturing wastewater by electrocoagulation , Desalination, 190 (2006) 201-211.
[10] Dubrawski K. L., Fauvel M., Mohseni M., Metal type and natural organic matter source for direct filtration electrocoagulation of drinking water, Journal of Hazardous Materials, 244 (2013) 135-141.
[11] Ulu F., Barışçı S., Kobya M., Sillanpää M., An evaluation on different origins of natural organic matters using various anodes by electrocoagulation, Chemosphere, 125 (2015) 108-114.

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Uranium levels in drinking tap and bottled waters in Cyprus

K. Philippou, I. Pashalidis*

University of Cyprus, Department of Chemistry, P.O. Box 20537, 1678 Nicosia, Cyprus
*Corresponding author: Email: pspasch@ucy.ac.cy

Abstract

Uranium is a (radio)toxic metal that is relative abundant and widespread in nature. Generally, the levels of uranium found in man's environment are relatively low, but natural processes and particularly anthropogenic activities may result in re-distribution of this element, which can cause serious contamination of waters with uranium. Consequently, it is of great importance to monitor uranium in waters and especially those used for drinking purposes to secure the biosphere and human health from adverse effects. The aim of this work was to determine uranium levels in drinking waters in Cyprus. Sampling included tap waters from different areas as well as local and imported bottled waters and the analysis has been performed by alpha-spectrometry after selective separation of uranium by cation-exchange. According to the results uranium concentration in the studied waters was found below the WHO guideline. Based on the experimental data the annual radiation exposure of Cypriot population resulting from water consumption has been assessed.

Keywords: uranium; 238U; 234U; drinking water; bottled water

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1. INTRODUCTION

Uranium is a ubiquitous, primordial radionuclide, the concentration of which in the environment strongly depends on the geological matrix. The concentration of uranium in acidic igneous rocks is significantly higher (up to 4 mg kg^{-1}) than in basic igneous rocks (~0.6 mg kg^{-1}) or even ultrabasic igneous rocks (~0.03 mg kg^{-1}). High uranium concentrations have been found in phosphate bearing rocks (up to 120 mg kg^{-1}, [4]) and deposits rich in natural organic matter (up to 250 mg kg^{-1}; [5]) and coal (up to 2000 mg kg^{-1}). However, anthropogenic activities such as mining, ore processing, agriculture, coal combustion, and nuclear fuel processing may lead to increased uranium levels in man's environment [6].

Uranium in waters results from the weathering of rocks and soil and uranium levels in groundwater systems vary considerably depending on the hosting geological formation and the presence of uranium ores [6]. The uranium concentration in groundwaters is governed by a number of processes, including dissolution and adsorption–desorption processes. Generally, higher uranium levels coincide with low pH and low adsorption capacity. In addition, in the presence of carbonate ions the mobility of uranium is enhanced due to the formation of very stable anionic U(VI)-carbonato complexes [13]. In addition, isotopic fractionation of the element is useful in identifying waters, tracing their hydrologic cycle and estimating mixing ratios and pollution budgets [10].

Uranium may enter bottled and tap water from naturally occurring deposits or as a result of human activities, such as mill tailings [6], emissions from the nuclear industry, the combustion of coal and other fuels, and the use of phosphate fertilizers that contain uranium. The Guideline for Drinking Water Quality of the World Health Organization gives a provisional value of 15 μg U L^{-1}

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[14] and in Germany bottled waters with uranium concentrations above 2 μg are not recommended for the preparation of baby food [6]. There no EU Guidelines for Drinking Water regarding the upper limit for uranium in drinking water, however uranium levels in drinking water need to be monitored and controlled by governmental authorities [6].

Knowledge of the uranium concentration in ground and surface waters is important in performing radiological impact assessment of various anthropogenic activities and aims to secure the increased standard of life in modern societies [8]. In Cyprus, a number of studies has been carried out in order to study uranium levels in seawater [1] and ground waters [3, 2]. However, there are no studies regarding uranium concentration in drinking tap and bottled waters.

In the present study uranium concentrations and the $^{238}U/^{234}U$ isotopic ratios have been determined in drinking tap and bottled waters in Cyprus. The analysis was performed by α-spectroscopy and the uranium concentration has been correlated to pH and other chemical parameters of the aqueous solutions. This study represents a comprehensive investigation on uranium levels in Cypriot drinking waters and aims to provide concentration values for uranium, a database for radiological impact assessment and point out the differences between different types of waters used for drinking purposes.

2. MATERIALS AND METHODS

A total of 26 samples of bottled water sold in Cyprus and 14 tap water samples from different tap water supplies on the island were collected and analyzed during September 2015 and May 2016. Prior any treatment the water samples to be analyzed were traced with 50 mBq ^{232}U tracer (NPL Laboratories).

The bottled samples had a label with all relevant information (pH, conductivity and main components). In addition, pH and EC (electrical conductivity) measurements were performed in our laboratory using a combined glass- and conductivity electrode, respectively and the uranium analysis was performed by α-spectroscopy. Uranium analysis in tap water samples was performed similarly, and included pH, conductivity and uranium analysis by α-spectroscopy.

α-spectroscopy

The α-spectroscopic analysis of uranium in selected groundwater samples was performed after pre-concentration and separation of uranium by cation exchange (Chelex 100 resin) and it's subsequent electrodeposition on stainless steel discs. The employment of high resolution α-spectroscopy allows an accurate determination of the activity of the ^{238}U and ^{234}U radioisotopes. In all cases, 1000 ml water samples were pre-treated by cation-exchange as described elsewhere [11, 2]. This pre-analytical procedure, which is selective for uranium [12], was carried out in parallel for every sample.

Alpha-spectroscopic analysis was performed using a high-resolution a-spectrometer (Alpha Analyst Integrated Alpha Spectrometer, Canberra) equipped with semiconductor detectors. Prior to sample measurement, the background was carefully measured under identical conditions and was found to be about 5 counts per day within the energy range of 3–8 MeV. Method calibration using cation exchange separation results in efficiency of 85%. The electrodeposition of uranium on stainless steel discs produced results with in excellent yields, generally over 99% [11]. The Minimum Detectable Activity (MDA) reached in the measurements was estimated to be about 1 mBq l^{-1} at the 95% confidence limit. The uncertainty of the uranium activity concentration and the $^{234/238}U$ ratio is around 10%.

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3. RESULTS AND DISCUSSION

3.1. Uranium concentrations in drinking waters

The uranium concentration data have been analyzed using a statistical software (JMP) and the results are graphically presented in the form of a box-plot in Figure 1. The data shown in Figure 1 correspond to tap water (TW) and bottled water samples (BW). The bottled water samples have been further separated into two groups, the local (BW_L) and the imported bottled waters (BW_I).

In all three cases the uranium concentration data (Figure 1) are log-normal distributed and the highest uranium levels are observed in the imported bottled waters. Specifically, the uranium concentration in imported bottled waters varies between 0.0005 and 8.0 μg U/L (median: 0.63 μg/L). Because uranium concentration in bottled water is determined by the geological origin and anthropogenic uranium emissions, and the bottled waters in Cyprus are mainly imported from EU countries (e.g. Greece), the uranium concentration values determined lie within the range obtained for European bottled waters (< 0.0005 μg/L < [U] < 16.0 μg/L) [16]. Nevertheless, even the highest values are below the current US EPA (2003) drinking water limit (30 μg/L) and the WHO guideline value of 15 μg U/L [14].

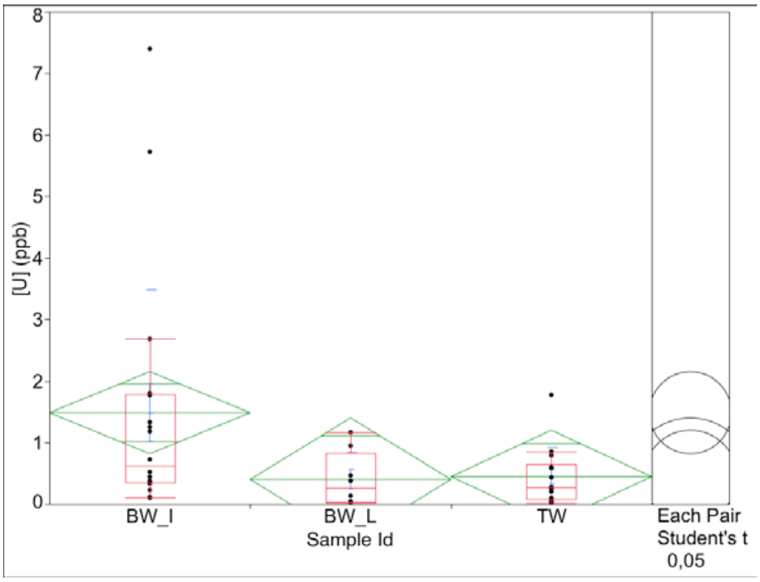


Figure 1. Uranium distribution in Cypriot to tap water (TW) and bottled local (BW_L) and imported (BW_I) water samples.

The uranium concentration in local bottled waters varies between 0.03 and 1.2 μg U/L (median: 0.26 μg/L) and are generally lower than the corresponding values determined in imported bottled waters. This is attributed to the origin of the local waters, which are ground waters hosted by igneous rocks of relatively low uranium content [2].

Regarding the uranium concentration in tap waters, the corresponding values vary between 0.02 and 1.8 μg U/L (median: 0.27 μg/L) and are generally lower than the corresponding values determined in European tap waters. This is because ground waters used as sources for drinking water have generally low uranium content and because domestic water use in Cyprus cities, to a large extent, comes from desalinated water.

From the radiological point of view none of the drinking water samples exceeds the suggested limits by WHO and EU [14, 17, 9] for alpha radioactivity in drinking water, which is 0.5 Bq l^{-1}. Regarding the chemotoxic effects, the guidance level for uranium in drinking water is 15 μg l^{-1}

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natural uranium which corresponds to 0.19 Bq l^{-1} ^{238}U radioactivity concentration. However, taking into account the limiting value for water for baby food (2 μg U/L , [18]), the uranium concentrations of some imported bottled waters are clearly above the recommended value.

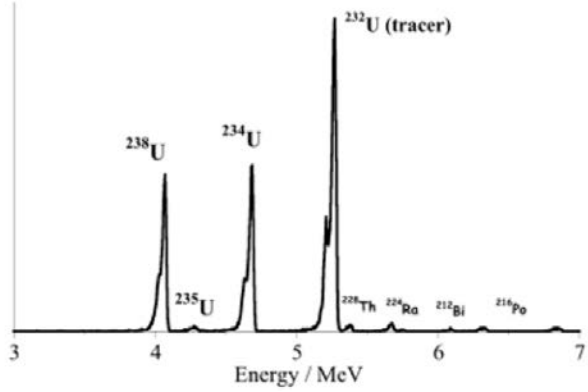


Figure 2. a-spectrum of a drinking water sample

The impact of man-made radioactivity is expected to be insignificant and contamination of the groundwater systems by anthropogenic sources can be excluded because of the absence of any activities that could lead to radioactive/uranium contamination of the drinking water sources. In addition, α-spectra of representative samples shown in Figure 2 indicate that the α-radioactivity in the studied samples is related basically to natural uranium, with the characteristic two main α-peaks of the ^{238}U and ^{234}U radioisotopes with energies of 4.198 and 4.776 MeV, respectively.

3.2 Correlation of the Uranium concentration with Physico-chemical Parameters

Figure 3 presents graphically a correlation between the uranium concentration ([U]) and the corresponding pH values in the studied waters, in the pH range between 7 and 8. The dotted line is obtained by linear regression of the experimental data and indicates statistically significant linear correlation (R= 0.6) and that uranium concentration in the studied waters decreases with increasing pH.

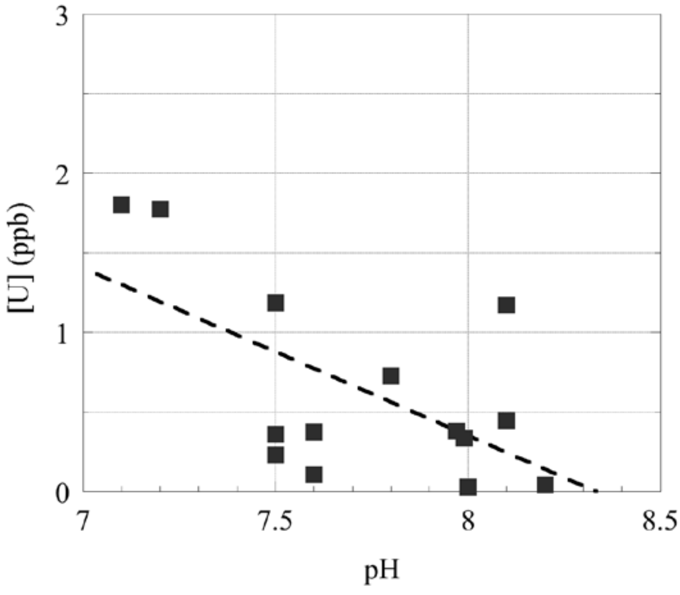


Figure 3. Correlation between uranium concentration in drinking water samples and solution pH.

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This seems to be in contradiction with results obtained from uranium solubility experiments, which show an increase in uranium solubility for pH > 6, because of the formation of very stable carbonate complexes (e.g. $UO_2(CO_3)_n^{(2n-2)-}$) [13, 20]. However, the uranium concentration in the respective waters is far below the solubility limit and depends only on the uranium amount dissolved from the corresponding geological matrix. Generally, decreasing pH results in the dissolution of soil minerals [7] and because uranium is adsorbed or forms solid solution with the soil mineral particles enters the aqueous phase upon mineral dissolution. Hence, decreasing pH results in increasing uranium concentration in solution.

In order to investigate the effect of bicarbonate concentration on the uranium levels in drinking waters the corresponding concentrations have been correlated with one another and the data are graphically summarized in Figure 4. There a relatively good correlation (R= 0.6) indicating the effect of the carbonate species on the uranium stabilization in solution, which is attributed to the formation of stable U(VI)-carbonato species [13, 20]. The formation of such cationic species competes surface adsorption reactions occurring in natural aquatic systems and results in increased uranium levels in the corresponding waters.

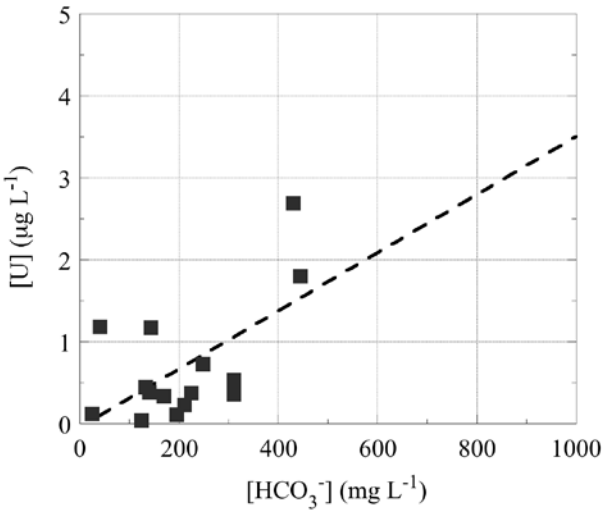


Figure 4. Correlation between uranium and bicarbonate concentration in drinking water samples.

3.3 Alpha-radiation dose rate calculation

Because uranium is the predominant alpha-radionuclide in the waters studied [19], we have used the highest uranium concentration to estimate the corresponding annual dose. The calculation was performed assuming a mean daily intake of 2 L of water and using the following equation

$$D = A \times I \times DCF \quad (1)$$

where D is the annual dose in mSv, A is the uranium radioactivity concentration in Bq/l, I is the mean annual water consumption (730 L) and DCF is the corresponding dose coefficient for ingested uranium (4.5 x 10-5 mSv Bq-1 ; IAEA, 1996).

The maximum annual dose calculated is below 0.002 mSv. This result, which corresponds to the highest uranium concentration in the drinking water samples, is below the guidance level recommended by the World Health Organization (WHO), which is equivalent to a committed effective dose of 0.1 mSv/y. According to WHO no deleterious radiological health effects are expected from consumption of drinking water if the concentrations of radionuclides correspond to committed effective doses below this value [14].

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4. CONCLUSIONS

Uranium levels in Cypriot drinking waters range between 0.0005 and 8.0 μg U/L and are below the limits suggested by WHO or US EPA. Generally, the highest uranium levels correspond to imported waters and this depends on the rock formations hosting the ground waters used as water source. Negative correlation between uranium concentration and pH in the waters under investigation indicates that uranium adsorbed or forming solid solution with the geological matrix enters the aqueous phase upon matrix dissolution with decreasing pH. On the other hand, increasing bicarbonate concentration is associated with increased uranium levels, which could be attributed to stabilizing effect of carbonate due to the formation of very stable U(VI)-carbonato species.

References

[1] Antoniou, S., Costa, C., Pashalidis, I., (2006), Alpha-radiometry of seawater by liquid scintillation counting. 270, 593-596.

[2] Charalambous C, Aletrari M, Piera P, Nicolaidou-Kanari P, Efstathiou M, Pashalidis I. (2013) Uranium levels in Cypriot groundwater samples determined by ICP-MS and α-spectroscopy. J Environ Radioact. 116, 187-192.

[3] Efstathiou , M., Kiliari T., Pashalidis , I. (2011) Uranium analysis in Cypriot groundwaters by total alpha-radiometry and alpha-spectroscopy. Radiat. Measur. 46, 626–630.

[4] Kratz, S., Schnug, E., 2006. Rock phosphates and P fertilizer as sources of U contamination in agricultural soils. In: Merkel, B., Hasche-Berger, A. (Eds.), Uranium in the Environment. Springer-Verlag, Berlin, pp. 57–67

[5] Lee, M.H., Choi, G.S., Lee, C.W., Shin, H.S., 2001. Concentrations and activity ratios of uranium isotopes in the groundwater of the Okchun Belt in Korea. Journal of Environmental Radioactivity 57 (2), 105–116

[6] Birke, M., Rauch, U., Lorenz, H., Kringel, R. Distribution of uranium in German bottled and tap water. Journal of Geochemical Exploration 107 (2010) 272–282

[7] Bruno, J., Wersin, P., Stumm, W., (1992), On the influence of carbonate in mineral dissolution: II. The solubility of $FeCO_{3(s)}$ at 25 ^{o}C and 1 atm total pressure. Geochim. et Cosmochim. Acta, **56**, 1149–1155.

[8] Chau, N.D., Michalec, B., (2009), Natural radioactivity in bottled natural spring, mineral and therapeutic waters in Poland. J. Radioanal. Nucl. Chem. **279**, 121–129.

[9] Desideri, D., Roselli, C., Feduzi, L., Meli, M.A., (2007), Radiological characterization of drinking water in Central Italy. J. Environ. Radioact. **87**, 13 – 19.

[10] Ivanovich, M., Harmon, R.S., (1992), Uranium-series disequilibrium: applications to earth, marine and environmental sciences. Clarendon Press, Oxford, p. 910.

[11] Killiari, T., Pashalidis, I., (2010), Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation- exchange. Radiat. Measurem., **45**, 966–968.

[12] Killiari, T., Pashalidis, I., (2012), Selective separation of actinyl(V,VI) cations from aqueous solutions by Chelex-100. Radiochim. Acta, 100, 439–443.

[13] Konstantinou, M., Pashalidis, I., (2004), Speciation and spectrophotometric determination of uranium in seawater. Medit. Mar. Sci., **5,** 55-60.

[14] World Health Organization, (2006), *Guidelines for Drinking Water Quality*, first addendum to third edition, Volume **1** Recommendations.

[15] United States Environmental Protection Agency (US EPA), 2003. National Primary Drinking Water Standards. U. S. Environmental Protection Agency, Office of Water, Washington D. C., EPA 816-F-03-016. - Online: http://www.epa.gov/ safewater/consumer/pdf/mcl.pdf (November 2006).

[16] EGS (EuroGeoSurveys) Geochemistry Expert Group, 2010. European Groundwater Geochemistry. Part 1: Bottled Water. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, Germany.

[17] EU Guidelines for Drinking Water, 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities, L 330, 5.12.1998, 32.

[18] MinTafWV, 2006. Vierte Verordnung zur Änderung der Mineral- und Tafelwasser-verordnung. Bundesgesetz-blatt, Bonn, Teil I 2006 (56), 2762–2763.

[19] Tsiaili, A., Kiliari, T., Pashalidis, I., 2011. Seasonal variation of the alpha-radioactivity concentration in natural water systems in Cyprus. Radiat. Meas. **46**, 145-148.

[20] Pashalidis, I., Czerwinski, K.R., Fanghaenel, Th., Kim, J.I., (1997), A Study of Solid-Liguid Phase Equilibria of Pu(VI) and U(VI) in Aqueous Carbonate Systems. Radiochim. Acta, **76**, 55-62.

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Inactivation of *Escherichia coli* in water by combined process of silver nanoparticle (AgNP) and UV radiation

M. A. Zazouli[1], M. Yousefi[2*], Y. Kor[3], M. Roohafzaee[2], F. Ghanbari[4]

[1] Department of Environmental Health Engineering, Faculty of Health and Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran.
[2] Department of Environmental Health Engineering, Student Research Committee, Mazandaran University of Medical Science, Sari, Iran.
[3] Department of Water and Wastewater Engineering, Gomishan Health Center, Golestan University of Medical Science, Gorgan, Iran.
[4] Department of Environmental Health Engineering, Student Research Committee, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran.
*Corresponding author: Email: maryam_u3fi7@yahoo.com

Abstract

The purpose of this research were to study of effectiveness of new technologies such as combined process of silver nanoparticle (AgNP) with UV radiation on *E. coli* inactivation as a water microbial pollution index and effects of some parameters on its efficiency. AgNP with average diameter of 20nm was used in the presence or absence of UV light for disinfection. Results showed that the disinfection efficiency of the UV and silver nanoparticles (UV+AgNP) combined process) is more than that of the catalyst (AgNP). The efficiency decreased with increasing the colony densities. The removal efficiency increased with increasing the catalyst dose, and contact time. It is concluded that the removal efficiency of E.coli by silver nanoparticles increases under the UV light.

Keywords: Escherichia coli; combined process; silver nanoparticles; UV radiation; water disinfection

1. INTRODUCTION

Disinfection is the most important stages in water treatment to ensure the water is free of pathogenic microbes that might cause waterborne diseases [1]. Waterborne health risks include cholera, typhoid, diarrhea, intestinal worms, trachoma, schistosomiasis and legionella disease [2]. So far, various chemical disinfection methods such as chlorination had been widely used [3]. The advantage of this method is inexpensive, lower operating cost in a wide range of pH and adequate residual effect [4-6]. Nevertheless, the main disadvantages of chlorination is production of toxic byproducts like trihalomethanes, haloacetic acids and other dissolved organic halogens as potential human carcinogens even at low concentration and also poor inactivation efficiency of spores, cysts and some viruses at low dosages used for bacterial coliform removal [7].

To date, over 500 DBPs have been identified in finished drinking water. The speciation and amounts of DBP produced are a function of the oxidizing agent used and reaction conditions [8]. Coleman *et al*. [9] have reported that a low concentration of common DBPs in water, such as haloacetic acid (60 ppb) and trihalomethanes (80 ppb), might cause serious congenital cardiac defects in human beings following prolonged consumption. For these reasons, various chemical-free water disinfection technologies without the formation of DBPs have become highly sought in recent years [10]. Chlorination incorporated with ozonation has greatly improved the disinfection efficiency for all pathogens of concern like bacteria, viruses and the cyst forming protozoan

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parasites as well as enhancement of water quality by removing toxicity and mutagenicity. However, the contradictory microorganism regrowth potential and high cost of ozonation have restricted it from being widely employed [7].

Consequently, for select a suitable water disinfectant need to consider the water quality objectives in terms of technical reliability, economic and environmental criteria. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly improved using products and processes resulting from the development of nanotechnology [11]. In recent years, nanoparticles have been the focus of considerable attention in a wide range of research areas, including especially environmental issues [12].

Nanosilver are the most widely commercialized nanoparticles that are used as antimicrobials [13]. Li *et al.* indicate three possible antibacterial mechanisms of silver nanoparticles: (1) Adhesion of nanoparticles to the bacteria surface, altering the membrane properties. The small size and extremely large surface area of nanoparticles enables them to make strong contact with the microorganism surface; (2) Silver nanoparticles penetrating inside the bacterial cell, resulting in DNA damage; (3) Dissolution of silver nanoparticles releases antimicrobial Ag^+ ions which can interact with sulphur-containing proteins in the bacterial cell wall, which may lead to compromised functionality. This phenomenon is often considered as the main mechanism of the antimicrobial activity of silver nanoparticle [14].

Although the antibacterial mechanisms of nanoparticles somewhat known [15-19], but there is still questions about their effectiveness in destroying pathogens and the possibility of their use for water disinfection. Therefore, the purposes of this research were to study of effectiveness of a new technology such as combined process of silver nanoparticles and UV on E.Coli inactivation as a water microbial pollution index and effects of some parameters on its efficiency.

2. MATERIALS AND METHODS

2.1. Materials

The catalyst employed in this work was silver nanoparticles (20 nm primary particle size, supplied by USNano Inc). E. coli cells ATCC 25922 (PTCC 1399) were supplied by Persian type culture collection. Tryptic Soy Agar (TSA) and Tryptic Soy Broth (TSB) were supplied by MERC Germany.

2.2. Cell Culture, Medium Preparation and Bacterial Counting

E.coli was cultured according to the center guidelines. Briefly, a single colony of E. coli was taken from refrigerated stock and precultured in 20 mL Tryptic Soy Broth (TSB) medium by incubation for 24 h at 37 C. Then it was transferred into TSA and incubated for 24 h at 37 C. The top of each colony was touched with a sterile loop and the growth was transferred into a tube containing 4 to 5 ml of distilled water. The cell concentrations were determined by comparing the cell density to 0.5 McFarland standards using UV/vis spectrophotometer towards an equivalent optical density of 0.1 at 620nm with regard to the calibrated standard cell suspensions in distilled water. To standardize the inoculums density for a susceptibility test, $BaSO_4$ turbidity standard, equivalent to a 0.5

McFarland standards was used. A 0.5 McFarland standard was prepared as described by Garcia [20]. To obtain required cell suspensions, the stock was serially diluted in distilled water. This results in a suspension containing approximately 10^3, 10^4 and 10^5 CFU/ml. Bacterial concentrations of these dilutions were confirmed by the standard plating method in triplicates on Tryptic soy agar. Samples were plated in triplicate. Following overnight incubation at 37 ^oC colonies were visually identified and counted.

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2.3. Experimental Procedure

Disinfection experiments were carried out in deionized/distilled water. All glassware used in these experiments was washed with distilled water, and then autoclaved at 121 ^{o}C for 15 min. AgNPs was suspended in water with 30 min of pre-sonication to disperse the particles uniformly. The characteristics of silver nanoparticles were determined by SEM, TEM and XRD analysis. A 6 W UV-C lamp, 30 cm in length with maximum emission at 254 nm, was installed 5 cm above the samples surface and the light intensity was 1.8 w/m^2 measured by a radiometer at 200 to 400 nm (Hagner ECL-X). All analyze were made according to the standard methods [21].

In these experiments, the photochemical cell consisted of sterile 250 ml beakers and magnetic stirrers that used for stirring the samples. The temperature of reactors was controlled at 20 ^{o}C. In the first phase of run, the beakers were filled with 200 ml of polluted water and in separate stages were contacted with UV, nanosilver and combination of them. In the examinations various parameters such as E.coli concentration (10^3,10^4,10^5 CFU/mL), amount of AgNP (0.05, 0.1, 0.2 and 0.4 mg/L) and time (10, 20, 40 and 60 min) were studied.

2.4. Statistical Tests:

Kolmogorov-Smirnov test was used to assess the normality of the data. If the is *greater* than 0.05, it indicates that the data are normal. Then, T-Test and ANOVA parametric tests used for statistical analysis.

3. RESULTS AND DISCUSSION

3.1. Nanoparticles characteristics

Silver nanoparticles were characterized by SEM (Figure 1), TEM (Figure 2) microscope and XRD analysis (Figure 3). Silver nanoparticles had a purity of 99.99%, particle size of 20 nm, the surface area of 18-22 m^2/gr and density of 10.5 gr/cm^3 and black color.

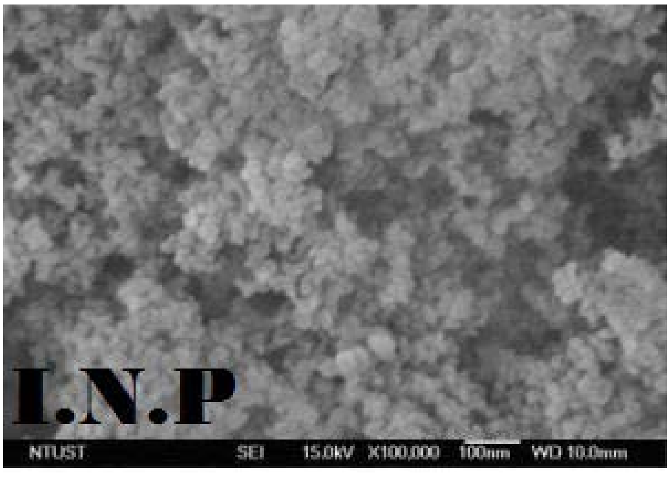


Figure 1. Scanning electron microscopic (SEM) images of the AgNPs

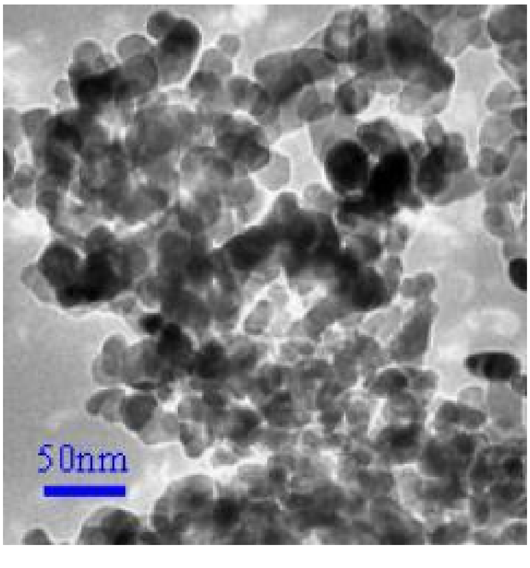


Figure 2. Transmission electron microscopic (TEM) images of the AgNPs

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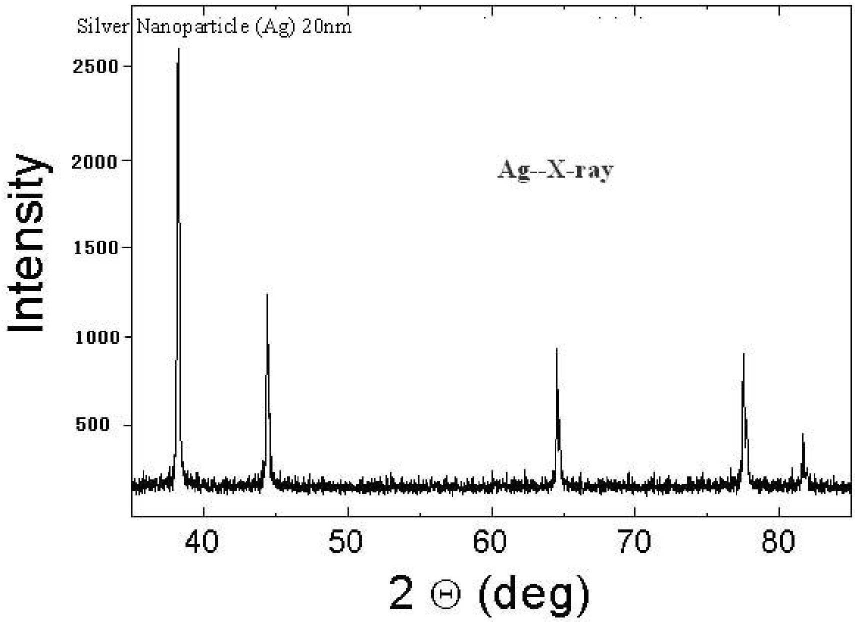


Figure 3. X-ray diffraction (XRD) of the AgNPs

3.2. Kolmogorov-Smirnov Test

Kolmogorov-Smirnov test was used to assess the normality of the data. The results of test showed that the data was normal($P_{value} > 0.05$). Therefore parametric tests (T-Test and ANOVA) were used. Results of the normality test are given in **Table. 1**. As can be seen, P-value is greater than 0.05. It indicates that data was normal. So ANOVA test was used.

Table 1. Kolmogorov-Smirnov test for assess the normality of photocatalytic process (UV+ AgNP) data

		Effect of UV& AgNP	Effect of E.Coli with AgNP+UV	Effect of AgNP concentration
N		12	12	20
Normal Parameters[a,,b]	**Mean**	73.4292	99.1067	74.6060
	Std. Deviation	20.27422	1.53047	20.15108
Most Extreme Differences	**Absolute**	0.158	0.387	0.192
	Positive	0.101	0.280	0.112
	Negative	-0.158	-0.387	-0.192
Kolmogorov-Smirnov Z		0.547	1.340	0.861
Asymp. Sig. (2-tailed)		0.926	0.055	0.449

a.Test distribution is Normal.

b. Calculated from data.

3.3. Effect of UV irradiation on the efficiency of AgNPs

Three series of process were carried out to perform this experiment. In all of three experiments a fixed number of colonies per milliliter (10^5) was used. In the first experiment, the bacteria have been exposed to UV without AgNPs. In the second experiment, the samples have been exposed to the AgNPs without UV. In the third experiment, samples have been exposed to the UV and AgNPs together. A silver nanoparticles concentration of 0.1 mg/L was used. The efficiency of disinfection in all experiments was determined in 10, 20, 40 and 60 minutes. The pH was adjusted at the natural range (7.5±0.5) in all experiments. The efficiencies of bacterial inactivation in different times are illustrated in Figure 4.

As shown in this Figure, efficiency of UV is lower than AgNPs. Also the combined process (UV+ AgNP) is more effective than only UV and only AgNP. The result of this study corresponds with the data given by Noroozi *et al* [22] and Zazouli *et al* [23] that although they used ZnO and TiO_2 nanoparticles, respectively.

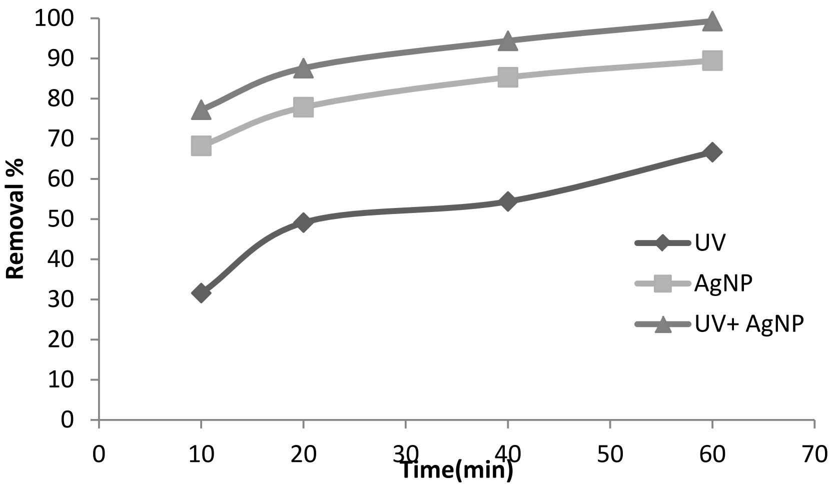


Figure. 4. The effect of AgNPs and UV on E.coli inactivation efficiency (Initial bacterial population: 10^5 CFU/mL)

To ensure that the bacteria population without the presence of light and nanoparticle is changing over time or not, blank sample like real sample was investigated that any changes not observed in the number of bacteria. Due to the lack of inactivation of bacteria, blank sample was not presented in the chart. As shown in Figure 4, inactivation of E.coli with AgNPs increased in the presence of UV light. Finding indicated that maximum efficiencies in 60 minutes of UV, AgNP and UV+nAg were 66%, 89% and 99%, respectively. AgNP is excited in presence of UV, and an electron from the valence band migrates to the conduction band, leaving a hole in the valence band and AgNP acts as an oxidizing agent. Electron pair production is important for oxidation process. In this process, water molecules divided to OH^- and H^+ radicals with a hole. Thus dissolved oxygen molecules with H^+ that generated at the beginning of the reaction form a hydrogen peroxide radical (OH^{2-}). This radical react with bacteria. Moreover, the nano scale particles have an extremely large relative surface area, thus increasing their contact with bacteria and vastly improving oxidation efficiency [12, 24].

In this study, increasing the contact time from 10 to 60 min, the inactivation of bacteria increases. So that in the presence of UV light and AgNPs, inactivation efficiency increases from 77% in 10 min to 99.31% in 60 min. Although inactivation efficiency increased with increasing the

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time, this trend is not too high after 20 min. Miranzadeh *et al* [18] investigated the effect of silver nanoparticles on the coliforms removal and water disinfection and showed that while increasing the time in all concentrations, the removal of probable coliforms ascends. Their results are in accordance with the findings of this study.

Miranzadeh *et al* [18] showed that after 100 min contact time in the 0.06 mg/L Silver concentration, the maximum removal efficiency was observed (92.41%). Also ANOVA test showed that there was a meaningful relationship between time and E.coli removal. Noroozi *et al* [22] studied the photocatalytic removal of Escherichia Coli by ZnO. They reported that the efficiency of UV, ZnO and UV/ZnO process in inactivation of 1000 CFU/mL of E.coli was 70%, 90% and 100%, respectively. Whereas in this study, the maximum efficiency of UV process in inactivation of E.coli is 66%. The reason for this difference is the number of bacteria. The number of bacteria in this study is 10^5 per milliliter, but in Noroozi *et al* [22] study was 10^3 per milliliter.

The comparison of the effect of UV process, AgNPs and UV and silver nanoparticles combined process (UV+ AgNP) showed that the removal efficiency of UV process is lower than AgNPs and both of them individually is lower than combined process. The study of the interaction effect of three processes with LSD test (95% Confidence intervals) showed that effect of UV as compared with AgNPs and UV+ AgNP is significant ($P_{value} < 0.05$), but the comparison of AgNPs process with UV+ AgNP process is not significant ($P_{value} > 0.05$). However disinfection efficiency of combined process (UV+ AgNP) is more than only catalyst (AgNPs). This efficiency difference is about 9-10% in all times.

3.4. Effect of bacterial population

The UV and silver nanoparticles combined process (UV+ AgNP) was performed with different bacteria concentrations (10^3, 10^4 and 10^5 CFU/mL) to study the effect of bacterial population on inactivation efficiency. The pH was adjusted at the natural range (7.5±0.5) in all experiments. The contact time was 10, 20, 40 and 60 minutes. Figure 5 shows the effect of initial bacterial population on the inactivation efficiency of E.coli under optimum conditions. The silver nanoparticles dosage was 0.2 mg/L in these experiments. As shown in Figure 5, inactivation efficiency is 100% when bacterial populations are lower than 10^5 CFU/mL.

The results indicated that the inactivation efficiency decreased with increasing the number of colonies. But statistical test using LSD test showed that their effect is not significant in two consecutive concentrations ($P_{value} > 0.05$). However disinfection efficiency with 10^5 CFU/mL E.coli was lower than when the number of colonies was 10^4 CFU/mL and 10^3 CFU/mL. Disinfection efficiency was 100% when bacterial population was 10^4 CFU/mL and 10^3 CFU/mL. The effect of bacterial population is significant only between 10^3 CFU/mL and 10^5 CFU/mL ($P_{value} < 0.05$). Due to an increase in bacterial density decreases the contact with light and AgNPs. So researchers preferred that continue the experiments with the high number of colonies in order that methods could be comparable.

However the antimicrobial properties of silver compounds and silver ions have been historically recognized and applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment. But the mechanism of toxicity is still only partially understood. Silver ions interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes and leading to the production of reactive oxygen species (ROS). It was also shown that Ag ions prevent DNA replication and affect the structure and permeability of the cell membrane. Silver ions are also photoactive in the presence of UV irradiation, leading to enhanced UV inactivation of bacteria and viruses. It is hypothesized that complexation of Ag with cysteine accelerates photodimerization of viral DNA contributing to a synergistic effect observed in inactivation of Haemophilus influenzae phage and MS2 phage [25].

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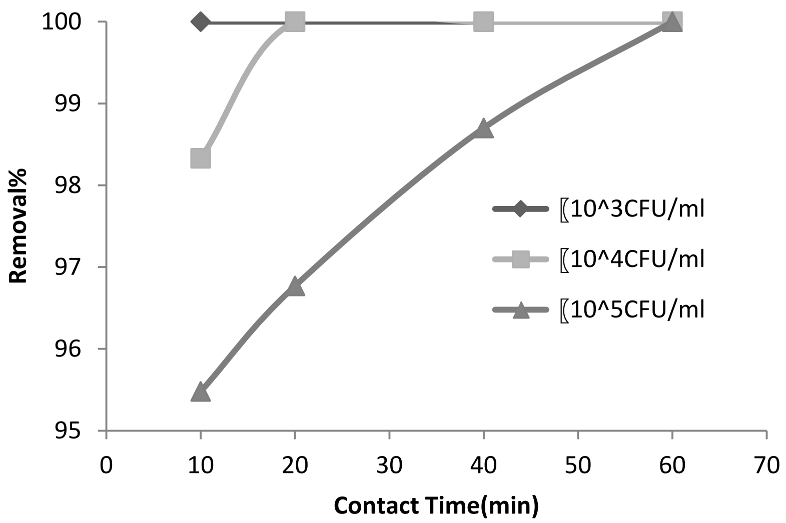


Figure 5. Effect of initial bacterial population on the combined process (UV+ AgNP) inactivation efficiency of E.coli (AgNPs dosage: 0.2 mg/L)

To date, several mechanisms have been postulated for the antimicrobial property of silver nanoparticles: (1) adhesion of nanoparticles to the surface altering the membrane properties. silver nanoparticles have been reported to degrade lipopolysaccharide molecules, accumulate inside the membrane by forming "pits", and cause large increases in membrane permeability; (2) silver nanoparticle penetrating inside bacterial cell, resulting in DNA damage; (3) dissolution of AgNPs releases antimicrobial Ag ions. Physicochemical properties play an important role in the antimicrobial activity of AgNPs. In general, particles of less than 10 nm are more toxic to bacteria such as Escherichia coli and Pseudomonas aeruginosa [25].

3.5. Effect of nanosilver dosage

Experiments were carried out with various silver nanoparticles dosage (0.05, 0.1, 0.2 and 0.4 mg/L) in order to investigate the effect of AgNPs dosage on the inactivation efficiency of the UV and silver nanoparticles (UV+AgNP) combined process. The number of colonies was 10^4 CFU/mL in these experiments. The results of this experiments presented in Table 2. As can be seen in this table, the inactivation efficiency of processes was 100%, when the AgNPs dosage was more than 0.05 mg/L. even after 40 min the inactivation efficiency of bacterial was 100% with 0.05 mg/L AgNPs dosage. So the other experiments performed with more number of colonies.

The comparison of the effect of different dosages of silver nanoparticles on disinfection efficiency was shown in Figure 6. the minimum, average and maximum efficiency of the combined processes with different dosage of AgNPs was presented in Table. 3. As can be seen in this table, the minimum and maximum of efficiency with 0.05 mg/L of AgNPs dosage are 42% and 82%, respectively. But its comparison with UV process without catalyst is not significant ($P_{value} >$ 0.05). While increasing the contact time and AgNPs dosage, minimum, average and maximum of efficiency ascends. Efficiency was 100%, when the AgNPs dosage and time was 0.4 mg/L and 20 min, respectively.

Statistical analysis showed that the efficiency of combined process with 0.05 mg/L of catalyst is not significant, as compared with only UV process ($P_{value} > 0.05$), but is significant, when more catalyst dosage was used ($P_{value} < 0.05$). Due to an increase in silver nanoparticles increases hydroxyl radical production since photo-excitation is also enhanced. As well as the contact with bacteria increases, so the efficiency increases. The differences between efficiency of combined

process with 0.1 and 0.2 mg/L of catalyst is not significant. However with increasing AgNPs dosage, the inactivation rate of bacteria increases. With increasing the AgNPs dosage, the probability of attachment of nanoparticles to the surface of bacteria, changing its membrane properties, its penetration into the cell and DNA damage and inactivation will be increase.

Rabbani *et al* [19] investigated the disinfection of synthetic polluted water with 30 to 180 mg/L of nanosilver without UV. They showed that disinfection of water with 30 to 180 mg/L of nanosilver without UV irradiation, the further coliforms removed when the concentration of AgNPs was raised, which corresponds with our study. But they reported that there was not a significant correlation between the AgNPs dosage and coliform removal (P_{value}=0.6). However, statistical analysis showed that this relation was significant in the present study.

The effect of nanoparticles on bacteria removal was studied by Gao *et al* [26]. They reported that regardless of the time, LC_{50} of nanosilver against the *Escherichia coli* and *Ceriodaphnia dubia* was lower than 112.14 and 6.18, respectively. However in this study, 0.1 mg/L of nanosilver with 10 min contact time cause to inactivation of 52% of *Escherichia coli*.

Table 2. The effect of nanosilver dosage on the efficiency of the UV and silver nanoparticle (UV+AgNP) process.

Number of Test	Initial Bacteria Population ($\times 10^3$CFU/ml)	AgNPs dosage (mg/L)	Time (min)			
			10	20	40	60
1	18	0.05	50%	83.33%	94.4%	100%
2	18	0.1	89.9%	100%	100%	100%
3	18	0.2	96.67%	100%	100%	100%
4	18	0.4	100%	100%	100%	100%

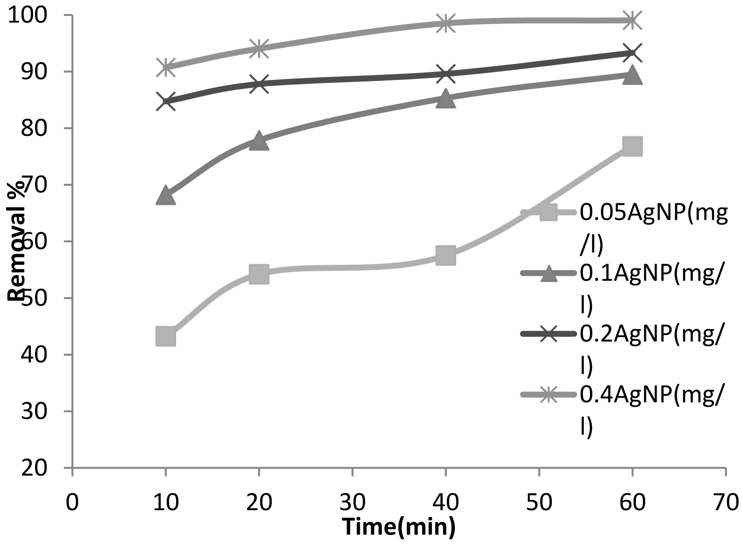


Figure 6. Effect of AgNPs dosage on the E.oli inactivation efficiency by the UV and silver nanoparticle (UV+AgNP) process (Initial bacterial population: 10^5 CFU/mL)

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Table 3. The effect of AgNPs dosage on the E.coli inactivation efficiency by the UV and silver nanoparticle (UV+AgNP) process. (Initial bacterial population: 10^5 CFU/mL)

Number of Test	AgNP dosage (mg/L)	Contact Time (min)											
		10			20			40			60		
		Min	Ave±SD	Max	Min	Ave±SD	Max	Min	Ave±SD	Max	Min	Ave±SD	Max
1	0.05	42.4	43.2±0.9	44.2	52.4	54.2±1.8	56	55.2	57.5±2.4	60	64.8	76.8±11	86.2
2	0.1	52	68.2±14	77.2	66	77.9±11	87.6	68	85.3±15	94.4	70.4	89.5±16.5	99.3
3	0.2	60.8	84.7±21	97.9	68	87.8±11	98.6	70.8	89.6±16.3	99.3	80	93.3±11.5	100
4	0.4	76.8	90.7±12.1	98.6	82.8	94.1±9.7	100	95.6	98.5±2.5	100	97.2	99.1±1.6	100

3.6. Effect of Time

The effect of contact time (10, 20, 40 and 60 min) on UV+AgNP process efficiency was shown in **Figure 7.** As can be seen, inactivation efficiency increased by increasing the contact time. The simulation effect of AgNPs and contact time on disinfection efficiency was presented in **Table 9**. Rabbani *et al* [19] showed that while the contact time increasing; the inactivation efficiency increase in all concentration of AgNPs. Statistical analysis showed that the efficiency of combined process with 0.05 mg/L of silver nanoparticles is a significant ($P_{value} < 0.05$) in different time, as compared with UV process. Only between 20 and 40 min is not a significant ($P_{value} > 0.05$). Also it's not significant at more concentration of AgNPs ($P_{value} > 0.05$). Due to the maximum activity of nanoparticles occurred at 0.05 mg/L concentration and 60 min contact time, but as regard statistical tests, it is not a significant in more dosages. However it has a rising trend. While the contact time increases, the contact of nanoparticles and bacteria, its penetration into cells, the rate of silver ions production and then the rate of bacterial inactivation increase [14].

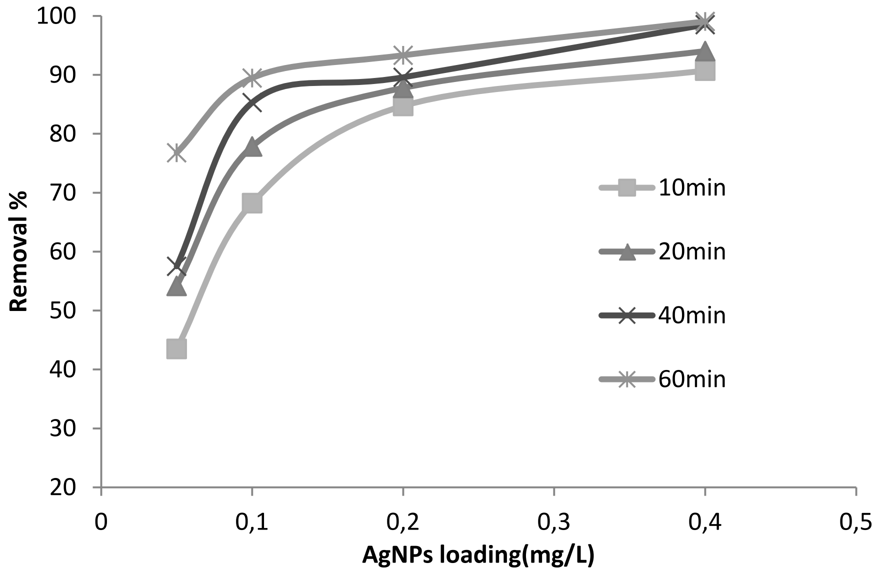


Figure 7. Effect of contact time on the E.coli inactivation efficiency by the UV and silver nanoparticle (UV+AgNP) process (Initial bacterial population: 10^5 CFU/mL)

4. CONCLUSIONS

The main purpose of this study was to evaluate the efficiency of the UV and silver nanoparticle (UV+AgNP) process in water disinfection. The final results of this study are summarized as below:

(1) The efficiency of the UV+AgNP process is more than of only AgNPs catalyst. In fact UV irradiation has a synergistic effect on efficiency of AgNPs. The difference of efficiencies is about 9-10% at various times.

(2) The minimum, average and maximum of inactivation efficiency increased by the increasing of AgNPs dosage and contact time. As the minimum, mean and maximum efficiency at dosage of 0.4 mg/L of AgNP and contact time of 20 min are 82.8, 94.1±9.7 and 100%, respectively.

(3) The statistical test showed that the efficiency of the UV+AgNP process at 0.05 mg/L dosage of AgNPs compared with UV only is not significantly different ($P_{value} > 0.05$). But it is significant ($P_{value} < 0.05$), when more AgNPs dosage was used. Because the increasing of dosage cause to increase the rate of photo-excitation and radical production. Furthermore its contact with bacteria and also efficiency increase.

(4) While bacterial population increases, the photocatalytic process efficiency will be decrease. When the bacterial population increases, the contact with light and catalyst and also photocatalytic products decreases.

Finally, we suggest that the disinfection efficiency of nanosilver in form of composite or coated on specific materials and zeolites; the Comparison between combined process with silver nanoparticles and silver ions; disinfection process with nanocatalyst compared with non-nano catalyst should be studied. Also there is a need to similar study for inactivation of microorganisms such as HPC bacteria, total coliforms, and fecal coliforms and fecal streptococci.

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Refrences

[1] Chong MN, Jin B, Saint CP. Bacterial Inactivation Kinetics of a Photo-Disinfection System using Novel Titania-Impregnated Kaolinite Photocatalyst. Chemical Engineering Journal. 2011;171(1):16-23

[2] Niven R. Investigation of Silver Electrochemistry Water Disinfection Applications. McGill University, Principles of Water and Waste Water Treatment. 2005.

[3] Salvato JA, Nemerow NL, Agardy FJ. Environmental Engineering: John Wiley & Sons; 2003.

[4] AGENCY EP. Water Treatment Manual:Disinfection. Irland2011.

[5] Huang JL, Wang L, Ren NQ, Liu XL, Sun RF, Yang GL. Disinfection Effects of Chlorine Dioxide on Viruses, Algae and Animal Planktons in Water. Water Res. 1997;31(3): 455–60.

[6] Junli H, Li W, Nenqi L, Li LX, Fun SR, Guanle Y. Disinfection Effects of Chlorine Dioxide on Viruses, Algae and Animal Planktons in Water. Water Res 1997;31(3): 455–60.

[7] Sun DD, Tay JH, Tan KM. Photocatalytic Degradation of E. Coliform in Water. Water research. 2003;37(14):3452-62.

[8] Richardson SD. New Disinfection By-Product Issues: Emerging DBPs and Alternative Routes of Exposure. Global NEST Journal. 2005;7(1):43–60

[9] H.M. Coleman, C.P. Marquis, J.A. Scott, S.S. Chin, R. Amal. Degradation of 1,4- Dioxane in Water using TiO_2 Based Photocatalytic and H_2O_2/UV Processes, Chemical Engineering Journal 113 (2005) 55–63.

[10] Chong MN, Jin B, Saint CP. Bacterial Inactivation Kinetics of a Photo-Disinfection System using Novel Titania-Impregnated Kaolinite Photocatalyst. Chemical Engineering Journal. 2011;171(1):16-23.

[11] Savage N, Diallo MS. Nanomaterials and water purification: opportunities and challenges. Journal of Nanoparticle Research. 2005;7(4-5):331-42.

[12] Nakata K ,Fujishima A. TiO_2 photocatalysis: Design and applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2012;13(3):169-89.

ISBN: 978-960-6865-94-7

[13] Bondarenko O1, Juganson K, Ivask A, Kasemets K, Mortimer M, Kahru A. Toxicity of Ag, CuO and ZnO nanoparticles to selected environmentally relevant test organisms and mammalian cells in vitro: a critical review. Arch Toxicol. 2013 Jul;87(7):1181-200.
[14] Reidy B, Haase A, Luch A, Dawson K, Lynch I. Mechanisms of Silver Nanoparticle Release, Transformation and Toxicity :A Critical Review of Current Knowledge and Recommendations for Future Studies and Applications. Materials. 2013;6(6):2295-350. PubMed PMID: doi:10.3390/ma6062295
[15] Morones JR1, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramírez JT, Yacaman MJ. The Bactericidal Effect of Silver Nanoparticles. Nanotechnology. 2005 Oct;16(10):2346-53
[16] Tugulea AM1, Bérubé D, Giddings M, Lemieux F, Hnatiw J, Priem J, Avramescu ML. Nano-Silver in Drinking Water and Drinking Water Sources: Stability and Influences on Disinfection By-Product Formation. Environ Sci Pollut Res Int. 2014 Oct;21(20):11823-31
[17] Gao J1, Youn S, Hovsepyan A, Llaneza VL, Wang Y, Bitton G, Bonzongo JC. Dispersion and Toxicity of Selected Manufactured Nanomaterials in Natural River Water Samples: effects of water chemical composition. Environ Sci Technol. 2009 May 1;43(9):3322-8.
[18] Miranzadeh MB, Rabbani D, Naseri S, Nabizadeh R, Mousavi SGA, Ghadami F. Coliform bacteria removal from contaminated water using nanosilver. KAUMS Journal (FEYZ). 2012;16(1):31-5.
[19] Rabbani D, Miranzadeh MB, Ghadami F, Zarjam R. Effect of Nanosilver Solution on Coliforms Removal in Synthetic Polluted Water. Journal of Applied Technology in Environmental Sanitation. 2013;3(1):15-20.
[20] Garcia L. Preparation of Routine Media and Reagents Used in Antimicrobial Susceptibility Testing. In: Clinical Microbiology Procedures Handbook. Garcia LS. 3rd ed. Washington, DC: ASM Press; 2010. p. 181-201.
[21] APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater. 22 ed: American Water Works Assn; 2012.
[22] Noroozi , R., M. Mehdinezhad, and zafarzadeh A, Photocatalytic Removal of Escherichia Coli by ZnO Activated by Ultraviolet-C Light from Aqueous Solution. Medical Laboratory Journal. 2011;5(2):52-61.
[23] Zazouli M, Ahanjan M, Kor Y, Eslamifar M, Hosseini M, Yousefi M. Water Disinfection Using Photocatalytic Process with Titanium Dioxide Nanoparticles. J Mazandaran Univ Med Sci. 2015;24(122):227-38.
[24] Reisner, D.E., Bionanotechnology II: Global Prospects. Vol. 2. CRC Press.; 2011:358.
[25] Li Q, ahendra S, Lyon DY, Brunet L, Liga MV, Li D, et al. Antimicrobial Nanomaterials for Water Disinfection and Microbial Control: Potential Applications and Implications. Water Research. 2008 11//;42(18):4591-602.
[26] Gao J, Youn S ,Hovsepyan A, Llaneza VL, Wang Y, Bitton G, et al. Dispersion and Toxicity of Selected Manufactured Nanomaterials in Natural River Water Samples: Effects of Water Chemical Composition. Environmental science & technology. 2009 May 1;43(9):3322-8. PubMed PMID: 19534153. Epub 2009/06/19.

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Phosphorus sorption by fine and coarse-grained sediments in the farm pond

N. Junakova, M. Balintova, M. Smolakova

Institute of Environmental Engineering, Faculty of Civil Engineering,
Technical University of Kosice, Vysokoskolska 4, 042 00 Kosice, Slovak Republic.
Email: natalia.junakova@tuke.sk

Abstract

Phosphorus availability is regarded as the most important factor for determining the water quality of lakes. When phosphorus enters surface waters in substantial amounts it becomes a pollutant, contributing to the excessive growth of algae and other aquatic vegetation and, thus, to the accelerated eutrophication of lakes and reservoirs. It may be transferred from the water column and adsorbed into sediments and accumulated in the bottom of rivers, lakes, or reservoirs. Phosphorus is relatively enriched in finer soil fractions, so it is perhaps expected that phosphorus adsorption is correlated with the clay content of soils and with the soil surface area.

The objectives of this study is to assess the ability of two sediment fractions, dredged from the Klusov farm pond (Slovakia), to retain phosphorus from overlying surface waters. The relationship between sediment properties and sorption parameters are also studied.

The results shown, that the finer sediment particles adsorbed phosphorus to a greater extent than do coarse particles. Fine-grained sediment with a higher specific surface area (8.85 m^2/g) adsorbed about 320 mg P/kg, in contrast to the coarse-grained sediment with a lower specific surface area (1.74 m^2/g), which adsorbed 160 mg P/kg. The results confirm, that the size distribution and specific surface area play an important role in the sorption properties of bottom sediments.

Keywords: phosphorus transport; sediment-water interface; reservoir

1. Introduction

Bottom sediments in reservoirs, lakes and rivers have been gaining increased attention worldwide due to their capacity to reserve or release different materials from the water column. Sediment can act both as sinks and sources for phosphorus, depending on environmental conditions, sediment properties as well as on antecedent nutrient loading and sorption capacity of the sediments [1]. Excessive phosphorus loads in surface water bodies lead to accelerated eutrophication of lakes and reservoirs. Phosphorus is strongly bound to sediments by anion adsorption reactions. These reactions probably account for the rapid removal of phosphorus from water that is in contact with lake sediments. Much of this adsorbed phosphorus is not easily desorbed, and the amount that is desorbable decreases with the age of the sediment-adsorbed phosphorus complex [2]. Understanding the processes leading to sorption and release of P by the sediments is of importance in controlling the trophic status of river or lake. Sediment properties such as particle size, surface area and geochemical composition are determining factors for the behaviour of sediments as a source or sink of phosphorus [3]. Different particle size and their cohesiveness has important chemical and physical implications for sediment quality [4]. Most of the phosphorus load to surface waters is particularly on fine-textured sediments, so it is perhaps expected that phosphorus adsorption is correlated with the clay content of sediments and with the sediment surface area [5-7].

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The aim of this study is to assess the ability of fine and coarse-grained sediments, dredged from the Klusov farm pond (Slovakia), to retain phosphorus from overlying surface waters.

2. MATERIALS AND METHODS

For this study, two sediment fractions - fine-grained S6 (< 63 μm) and coarse-grained S9 (> 63 μm) - taken from the Klusov farm pond (Slovakia) were used. The first one was sampled in the area of the dam because of the maximum deposition of clay and silt particles, mainly responsible for the transport of adsorbed phosphorus. The second one was sampled at the inflow to the reservoir due to the coarser sediments settling.

2.1 Sediment properties

For sediment characterization, granularity and specific surface area as basic physical parameters were defined.

Particle size distribution of sediment samples were conducted through a combination of dry sieve method and laser diffraction method (clay: <0.004 mm), silt: 0.004–0.063 mm, sand: 0.063-2.0 mm, gravel: >2.0 mm). Coarse-grained sediment sample was analysed by passing the dry composite sediment sample through a standard series of sieves with mesh sizes from 4 mm to 0.125 mm. Undersize particles were analysed by laser diffractometry using a Mastersizer 2000 (Malvern Instruments, UK) with a Hydro 2000S wet dispersion unit, capable of analysing particles between 0.02 and 2,000 μm. Fine-grained sediment sample was analysed using the same equipment. Measurement parameters were: pump speed - 2,800 rpm; ultrasonic - turned on for 5 min after sample addition.

Specific surface area (SSA) was estimated by low temperature gas adsorption using nitrogen gas (Quantachrome NOVA 1000e, USA) and subsequent application of Brunauer – Emmett – Teller isotherm.

The chemical composition of the sediments was determined by X-ray fluorescence method using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10,000 pulses.

2.2 Phosphorus sorption

After determining the basic physico-chemical sediment characteristics, the sorption process was observed.

Two grams of air-dried sediment samples were placed in 50 ml of 0.01M $CaCl_2$ containing 0, 5, 10, 30, 50, 75, 100 mg/L, as KH_2PO_4. The mixtures were agitated for 24 hours at a constant temperature until adsorption equilibrium was reached. Then supernatants were filtered through a 0.45-μm filter membrane. Phosphorus equilibrium concentration (C_e) of the supernatant was measured by the molybdovanadate method with acid persulfate digestion using a DR 890 portable colorimeter (Hach Lange) after an equilibrium time. The amount of P adsorbed by the sediment at equilibrium was calculated as the difference between the amount of P initially present in solution and the amount remaining at the end of the experiment (indirect method) using the formula (1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \qquad (1)$$

where q_e is the phosphorus content adsorbed or desorbed by sediment at equilibrium (mg P/kg), C_o is the initial P concentration in solution (mg/L), C_e is concentration of P in filtered solution after 24 hours of equilibration (mg P/L), m is the adsorbent/sediment mass (kg), and V is the volume of KH_2PO_4 solution (L).

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The percent sorption of P from aqueous solution at different initial concentrations for both sorbents (S6 and S9 sample) was calculated as follows (2):

$$\%\,\text{Sorption} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Physico-chemical sediment properties

The particle size distribution of sediments under 2,000 μm, analysed by laser diffractometry and characterized by grading curves, is presented in Figure 1. The results indicate that the clay/silt fraction dominate in fine-grained sediment sample (S6), with more than 95 % proportion of particle size below 0.063 mm. Coarse-grained sediment sample (S9) contains about 50 % of sand and gravel particles.

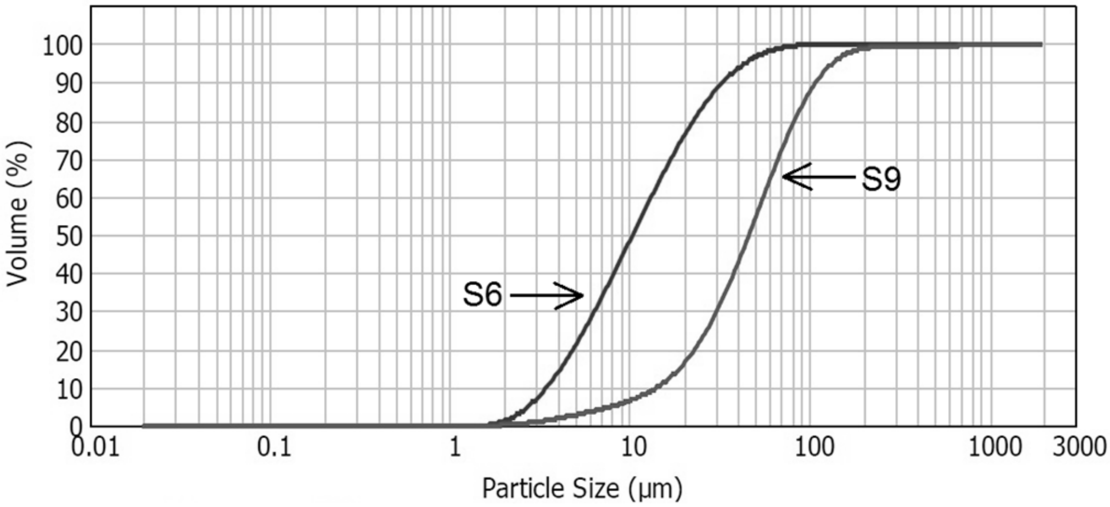


Figure 1. Particle size distribution measured for fine (S6) and coarse-grained (S9) sediments

Table 1 summarizes the specific surface area (SSA) and chemical composition of the sediments.

Table 1. Specific surface area (SSA) and chemical composition of the sediments

	SSA	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	CaO	P_2O_5
	m^2/g				(%)			
S6	8.85	68.56	18.01	5.15	2.40	2.95	1.10	0.26
S9	1.74	49.66	5.39	1.51	1.06	0.68	0.57	0.11

The SSA of fine-grained sediment is larger (8.85 m^2/g) in comparison with coarse-grained sediment with the SSA of 1.7 m^2/g. The chemical composition of the sediments obtained from XRF analysis reveals that SiO_2 and Al_2O_3 predominantly compose the sediment samples. Toxic

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compounds in sediments were not recorded. The total phosphorus content in collected sediment samples are diverse due to irregular sediment deposition in the reservoir and increase with the proportion of fine-grained particle fraction.

3.2 Phosphorus sorbed by fine-grained and coarse-grained sediment

The amount of P sorbed by fine-grained and coarse-grained sediment from solution containing 0, 5, 10, 30, 50, 75, 100 mg/L, as KH_2PO_4 and their sorption efficiency is shown in Tables 2 and 3, respectively.

The results demonstrated, that maximum sorption of P by fine and coarse-grained sediments were observed at P concentrations > 100 mg KH_2PO_4/L. At the highest adsorbate dose (100 mg KH_2PO_4/L), studied phosphorus sorption capacity was 322 mg/kg for fine-grained and 160.6 mg/kg for coarse-grained sediment (Figure 2).

Table 2. The phosphorus content sorbed by fine-grained sediment (S6) at equilibrium

Adsorbate dose (mg KH_2PO_4/l)	**C_0**	**$C_{e,\ S6}$**	**$q_{e,\ S6}$ (mg P/kg)**	**Sorption, S6 (%)**
	(mg P/L)			
0	0	0.13*	3.25*	-
5	1.18	0.14	26.01	98.90
10	1.6	0.20	34.90	95.51
30	6.36	0.53	145.86	93.79
50	11.12	1.13	249.73	91.00
75	17.68	1.99	321.90	73.43
100	23.87	11.0	322.05	54.51

Note: * desorption occurs

Table 3. The phosphorus content sorbed by coarse-grained sediment (S9) at equilibrium

Adsorbate dose (mg KH_2PO_4/l)	**C_0**	**$C_{e,\ S9}$**	**$q_{e,\ S9}$ (mg P/kg)**	**Sorption, S9 (%)**
	(mg P/L)			
0	0	0.08*	2.00*	-
5	1.18	0.26	22.99	84.02
10	1.6	0.50	27.56	73.67
30	6.36	2.77	89.68	57.59
50	11.12	6.46	116.59	42.61
75	17.68	12.36	132.90	30.50
100	23.87	17.5	160.62	27.23

Note: * desorption occurs

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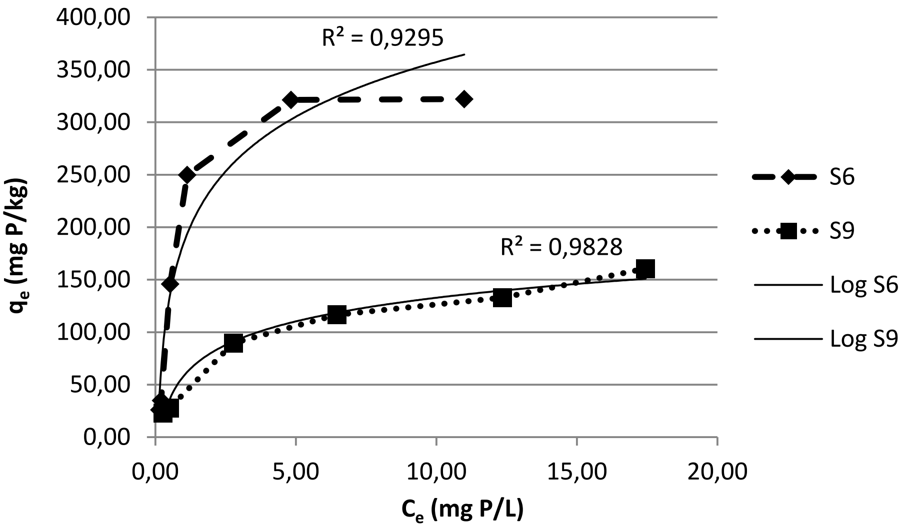


Figure 2. Phosphorus adsorption of fine (S6) and coarse-grained (S9) sediments in the farm pond

On the other hand, reservoir sediments indicated minimal P sorption at low P content. Furthermore, the release of phosphorus into solution was observed without the addition of adsorbate. The high logarithmic correlation was recorded, what also expressed the experimental data with the values of c*oefficient of determination* $R^2 \geq 0.92$. However, with the increasing adsorbate dose a linear P uptake was observed (Figure 3).

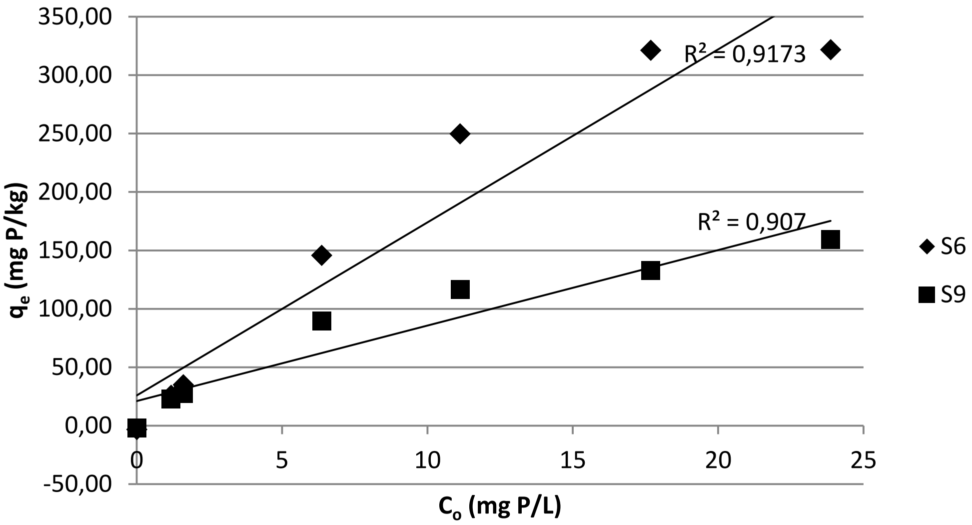


Figure 3. Relationship between adsorbate dosage and phosphorus content sorbed by sediments at equilibrium

These results are consistent with results by other researchers reporting that a larger particle size and specific surface area cause a smaller phosphorus sorption capacity [7,8].

Adsorption and desorption processes, that are universal phenomena existing on different interfaces in nature, affect not only the characteristics of sediment and water, but also the surrounding environment.

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4. CONCLUSIONS

In this research, the grain size, specific surface area and chemical composition of fine and coarse grained sediments in the Klusov farm pond was investigated. Subsequently, the ability of phosphorus sorption by these sediments was demonstrated.

The results showed, that finer sediment particles with the higher specific surface area adsorb phosphorus to a greater extent than do coarse particles. The phosphorus sorption capacity is probably also associated with mineral composition of sediments containing higher Fe and Al content in finer sediment particles. At low content of phosphorus input into solution, reservoir sediments indicated minimal P sorption. Furthermore, the release of phosphorus into solution was observed without the addition of adsorbate. Sorption efficiency of sediments decreased with the increasing of adsorbate dosage. At low adsorbate dosage the phosphorus sorption efficiency by sediments is high, whereas at high concentrations of the sorption agent the sorption process significantly stabilizes in terms of reaching the maximum sorption capacity of the bottom sediments.

Acknowledgements

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References

[1] Karstens, S., Buczko, U., Glatzel, U.S., 2015. Phosphorus storage and mobilization in coastal Phragmites wetlands: Influence of local-scale hydrodynamics. *Estuarine, Coastal and Shelf Science*, **164**, 124-133.

[2] National Research Council, 1993. *Soil and Water Quality: An Agenda for Agriculture*. National Academy Press, Washington D.C., USA.

[3] Shen, Z., Niu, J., Wang, X., Wang, H., Zhao, X., 2013. *Distribution and Transformation of Nutrients in Large-scale Lakes and Reservoirs. The Three Gorges Reservoir.* Springer-Verlag Berlin Heidelberg.

[4] Ongley, E., 1996. Chapter 13 - Sediment measurements. *Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes* (eds J. Bartram and R. Ballance), UNEP/WHO.

[5] Tamatamah, R.A., 2005. Phosphorus sorption in relation to soil grain size and geochemical composition in the Simiyu and Kagera river basins, Tanzania. *Tanzania Journal of Science*, **31 (2)**, 31-39.

[6] Rawlins, B.G., Turner, G., Mounteney, I., Wildman, G., 2010. Estimating specific surface area of fine stream bed sediments from geochemistry. *Applied Geochemistry*, **25**, 1291–1300.

[7] Xiao, Y., Zhu, X., Cheng, H., Li, K., Lu, Q., Liang, D., 2013. Characteristics of phosphorus adsorption by sediment mineral matrices with different particle sizes. *Water Science And Engineering*, **6 (3)**, 262-271.

[8] Wang, X. Y., Zhang, L. P., Zhang, H. S., Wu, X., Mei, D., 2012. Phosphorus adsorption characteristics at the sediment–water interface and relationship with sediment properties in FUSHI reservoir, China. *Environmental Earth Sciences*, **67 (1)**, 15-22.

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Rainwater tanks reliability analysis in Cyclades islands

E. Papagianni[1], P. Londra[2], A. Theocharis[3], E. Baltas[1*], V. A. Tsihrintzis[4]

[1] Department of Water Resources and Environmental Engineering, Faculty of Civil Engineering, National Technical University of Athens, 5 Iroon Polytechniou, 157 73, Athens, Greece.
[2] Department of Natural Resources Management and Agricultural Engineering, Agricultural University of Athens, 75 Iera Odos, 11855 Athens, Greece
[3] General Directorate of Sustainable Plant Production, Ministry of Rural Development and Food, Athens, Greece.
[4] Laboratory of Reclamation Works and Water Resources Management, School of Rural and Survey Engineering, National Technical University of Athens, Zografou, Greece.
*Corresponding author: Email: baltas@chi.civil.ntua.gr

Abstract

Rainwater harvesting is a worldwide spread sustainable non-conventional method which can be used to address the issue of water deficiency in Aegean islands and especially in Cyclades. In this study, a rainwater tank reliability analysis was conducted based on a daily water balance model to meet 30% and 50% of daily water demand of a 3- and 4-people household in 5 Cyclades islands. The reliability was defined as percentage of days in the time period studied when rainwater tank was able to supply a specific demand. Reliability in relation to rainwater tank size was determined for three different rainwater collection areas of 100, 200 and 300 m^2. The analysis of the results showed that reliability was strongly influenced by rainfall regime, roof area, tank size and total water demand satisfied by harvested rainwater.

Keywords: Cyclades islands; rainwater; tanks

1. INTRODUCTION

Greece has adequate water resources in general but also high spatial and time variations in availability, especially in Aegean islands. Cyclades are a typical example of intense water resources problems and their future may be threatened by overexploitation.

Rainwater harvesting is a practice of collecting rainwater from a) land catchment area, which can store the collected water in ditches, ponds, tanks and reservoirs, either for irrigation or to recharge groundwater aquifers, and b) from roof surface, which is used mainly in urban areas and water is stored either in above ground or underground tanks, aimed mainly for domestic use and irrigation of home gardens. Today, domestic rainwater harvesting has become increasingly important as a modern, relatively cheap and simple water saving technology, being one of the most promising alternative water supply options against the problem of increasing water scarcity and demand. It provides the possibility of increasing water reserves while allowing self-reliance and sustainability.

One of the main methodologies to determine the optimum size of rainwater tank is the water balance model (behavioural models) [1,2,3,4,5], which is applied either by using daily or monthly rainfall data.

One advantage of the behavioural methods is that they can measure several variables of the system over time, such as volumes of consumed and overflowed rainwater, percentage of days in which rainwater demand is met [6], etc. The main disadvantage of these methods is that there is no guarantee of similar results when using different rainfall data from the same region, as the

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simulation is based on a water mass balance equation [7]. Furthermore, another method being used, is sizing the water storage tank based on probability models (probabilistic models) [8,9,7,10].

All methodologies are based on recordings of local rainfall data used either directly as hydrological input data in the system or as input data for forecasting parameters required in a stochastic rainfall model. Overall, the capacity of rainwater harvest tanks cannot be formulated because is strongly influenced by several local variables, such as local rainfall, the collection surfaces, demand and the number of routes residents [11,12,5,13].

In Greece, it is imposed statutorily the construction of rainwater harvesting tanks in 27 Aegean islands, mainly small Cyclades and eastern Aegean islands. Furthermore, many attempts have already been made in Greece in order to set the necessary legal framework under which the collection of rainwater harvesting could be obtained along with the needed environmental and urban planning conditions. In addition, a recent study proposed the extension of that compulsory construction in other areas that belong to deficient or marginally deficient water districts such as Eastern Central Greece, Thessaly, Eastern Peloponnese, Crete and the rest of Aegean Islands [5,13]. The objective of this study is the evaluation of rainwater harvest tank reliability for domestic use in Cyclades islands. The level of reliability is tested in various tank sizes, using the method of daily water balance in 5 Cyclades islands to meet non-potable water demand of 3- to 4-people household.

2. MATERIALS AND METHODS

2.1 Study area

Daily rainfall data of 5 Cyclades islands within the period 1990-2012 were obtained from the Hellenic National Meteorological Service. The station selection criteria were: a) data availability and b) time series completeness.

2.2 Daily water balance method

A spreadsheet-based daily water balance model was developed considering daily rainfall, contributing catchment (roof) area, losses due to leakage, spillage and evaporation, storage (tank) volume and water uses. The water balance model equation used [4,5] is given as

$$S_t = S_{t-1} + R_t - D_t \qquad 0 \le S_{t-1} \le V_{tank} \tag{1}$$

or

$$S_t = S_{t-1} + C \cdot A \cdot P_{eff,t} - N_{cap} \cdot q \cdot \left(p/100 \right) \qquad 0 \le S_{t-1} \le V_{tank} \tag{2}$$

where S_t is the stored volume at the end of t^{th} day (m^3), S_{t-1} the stored volume at the beginning of t^{th} day (m^3), R_t the harvested rainwater volume during the t^{th} day (m^3), D_t the daily water demand (m^3) and V_{tank} the capacity of rainwater tank (m^3). C is the collection area runoff coefficient, A is the rainfall collection area (m^2), $P_{eff,t}$ is the daily effective rainfall depth at the end of t^{th} day (m), N_{cap} is the number of capita (residents), q the daily water use per capita and p the percentage of total water demand satisfied by harvested rainwater.

In the present study, the runoff coefficient was assumed equal to 0.9 and the daily effective rainfall was assumed equal to the daily rainfall minus a first flush equal to 0.33 mm [14] for improving the quality of harvested rainwater from concentrations of dust, leaves and bird droppings in rainfall collection area [5].

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Assuming a capacity of the rainwater tank (V_{tank}), the daily stored water in the tank was calculated using heuristic algorithms iteratively, allowing the excess water to overflow, and when the stored water is inadequate to meet the demand, then the public water supply is used to cover the water needs [5,13].

2.3 Reliability coefficient

The reliability coefficient (Re) enables the determination of rainwater tank efficiency for the demand levels studied. The coefficient Re of a rainwater tank is calculated as the ratio of the number of days when intended demand is fully met by the available stored rainwater (N_f) and the total number of days simulated (N_{tot}).

$$\mathrm{Re} = \frac{N_f}{N_{tot}} \cdot 100 \tag{3}$$

Accordingly, in this study the reliability coefficient is calculated using daily rainfall data records on a continuous time series for a simulation period of 22 years (N_{tot}=8030 days).

2.4 Data

Using the abovementioned methodology, the daily water balance model was applied in a spreadsheet of Microsoft Excel using the daily rainfall data of the period 1990-2012 for several different tank sizes, roof areas, number of residents and percentage of total demand to be fulfilled by rainwater tank.

A range of tank sizes from 5 to 50 m^3 were considered, which represent both usual and statutorily imposed sizes [5]. In regards to catchment area, roof areas equal to 100, 200 and 300 m^2 were considered, which represent achievable overall collection areas within islands studied. The water demand for non-potable use of a 3- and 4-people household was determined, assuming daily water use per capita 150 L/cap/day and percentage of total water demand to be fulfilled by harvested rainwater 30% and 50%. These percentages correspond to water use for toilet (~ 30%), bathroom-shower (20%-30%) or/and cloths and dishes washing (~ 15%) [5].

3. RESULTS AND DISCUSSION

The analysis of rainfall data from 5 rainfall stations, within the District of Cyclades, showed that the lowest mean annual rainfall value was observed in Santorini island (293 mm) and the highest one observed in Mykonos island (415 mm) (Table 1).

Table 1. Mean annual rainfall values (P), max ($N_{dd,max}$) and mean ($N_{dd,ave}$) values of the longest annual dry periods for the rainfall time series (1990-2012) of 5 stations studied.

Rainfall station	P (mm)	$N_{dd,max}$ (days)	$N_{dd,ave}$ (days)
Santorini	293	198	141
Naxos	343	176	132
Paros	377	200	143
Milos	383	169	129
Mykonos	415	171	131

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Also, the maximum ($N_{dd,max}$) and mean ($N_{dd,ave}$) values of the longest annual dry periods recorded for the rainfall time series of all stations studied, were determined and are presented in Table 1. The $N_{dd,ave}$ and $N_{dd,max}$ values ranged approximately from 4 to 5 months and from 6 to 7 months, respectivelly. Note that, dry period was defined as the period without any rainfall or effective rainfall less or equal to 1 mm.

Rainfall regime of these islands is similar and constitutes mainly of few high daily winter episodes among sort dry periods, followed by very long summer dry periods.

Figures 1-3 show the reliability curves for different tank sizes for 3-people household and 30% demand to be fulfilled by rainwater (i.e. total water demand 135 L/day) for three different roof areas 100, 200 and 300 m^2.

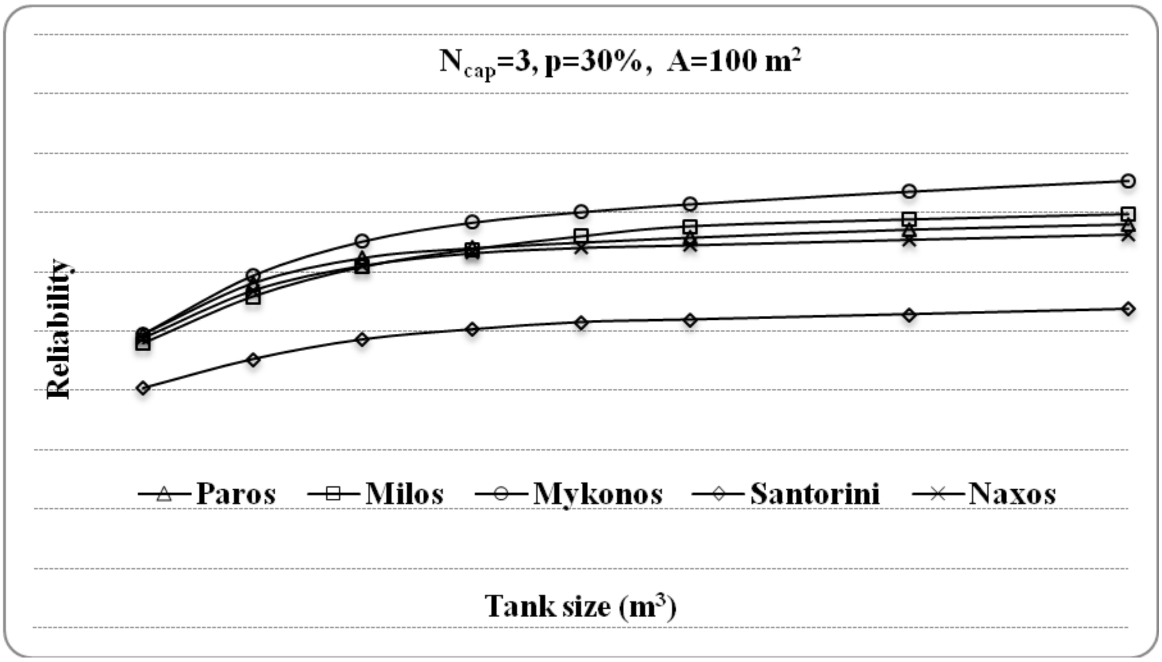


Figure 1. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 30% for 3-people household (135 L/day) with roof area of 100 m^2.

As shown in Fig. 1, low demand (135 L/day) - low roof area (100 m^2) scenario, reliability increases with the tank size and the maximum reliability of 75% can only be achieved for tank size of 50 m^3 in the case of Mykonos island. The lowest reliability values were observed in Santorini island ranging from 40% to 54% for tank sizes from 5 to 50 m^3, respectively.

Figure 2 shows the reliability curves for low demand (135 L/day) - medium roof area (200 m^2) scenario. Reliability ranges from 52% to 60% for tank size of 5 m^3 and reaches approximately the value of 90% for tank size of 20 m^3 in most islands studied with exception of Santorini since it needs 50 m^3 for 90% reliability.

The effect of roof area doubling (from 100 to 200 m^2) in reliability increase, is clearly shown in high tank size values since only them can store high daily rainfall values.

Evaluating Fig. 3, which shows the low demand (135 L/day) - high roof area (300 m^2) scenario, it is observed that reliability reaches 100% for tank sizes more than 30 m^3, with the exception of Milos which requires 50 m^3 and Santorini which never exceeds 95%. Reliability still stays low in low tank sizes.

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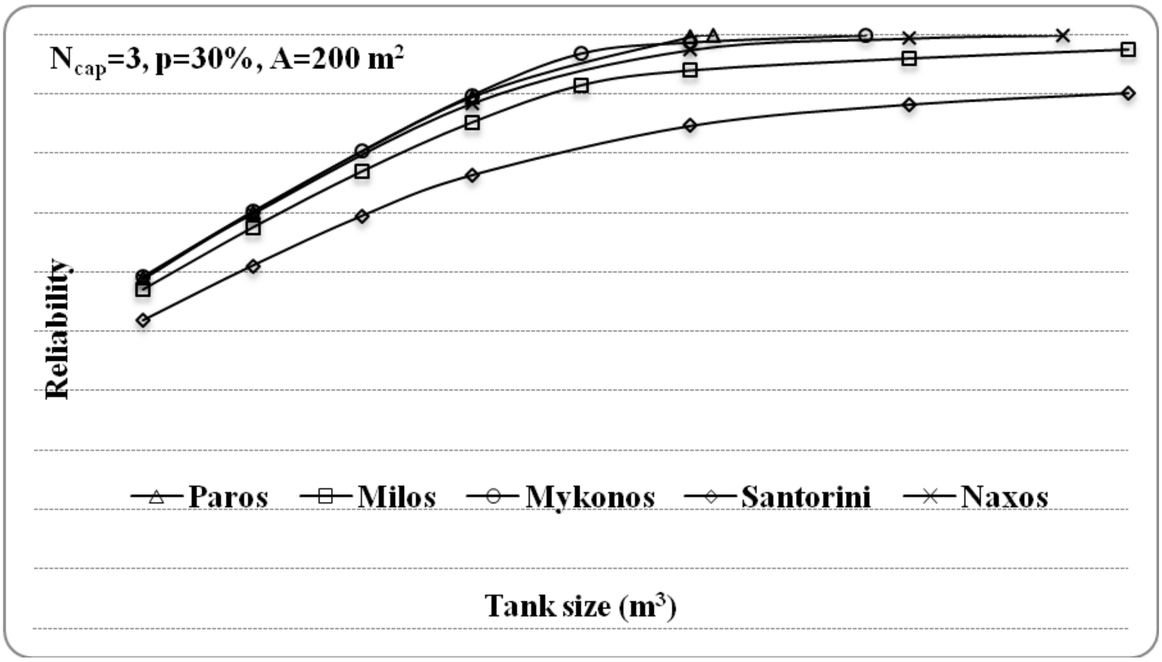


Figure 2. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 30% for 3-people household (135 L/day) with roof area of 200 m^2.

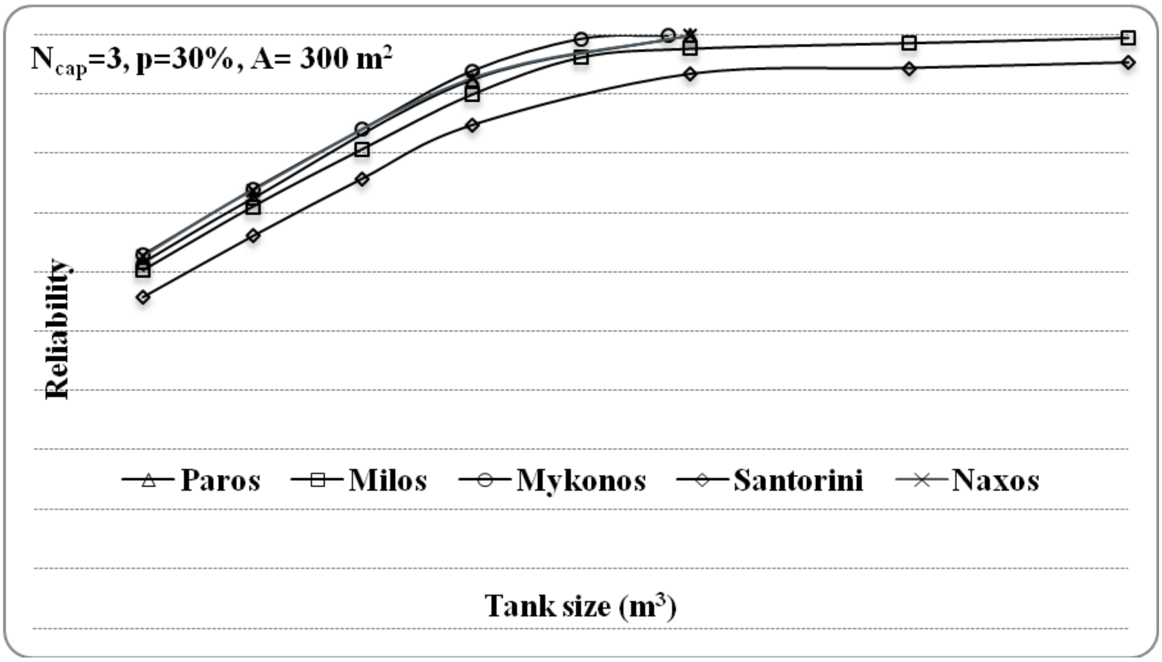


Figure 3. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 30% for 3-people household (135 L/day) with roof area of 300 m^2.

Figures 4-6 show the reliability curves for different tank sizes for 4-people household and 50% demand to be fulfilled by rainwater (i.e. total water demand 300 L/day) for three different roof areas 100, 200 and 300 m^2.

Figure 4 shows the reliability curves for high demand (300 L/day) - low roof area (100 m^2) scenario. It is obvious that for this scenario reliability increases negligible with the increase of tank

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size. The maximum reliability does not exceed 50% even with tank sizes of 50 m^3 in all islands studied. In particular, higher reliability values range from 35% to 49% in Mykonos and lower values range from 19 to 22% in Santorini. It has to be noticed that Mykonos has the highest annual rainfall (415 mm) and Santorini has the lowest one (293 mm) among the five islands studied.

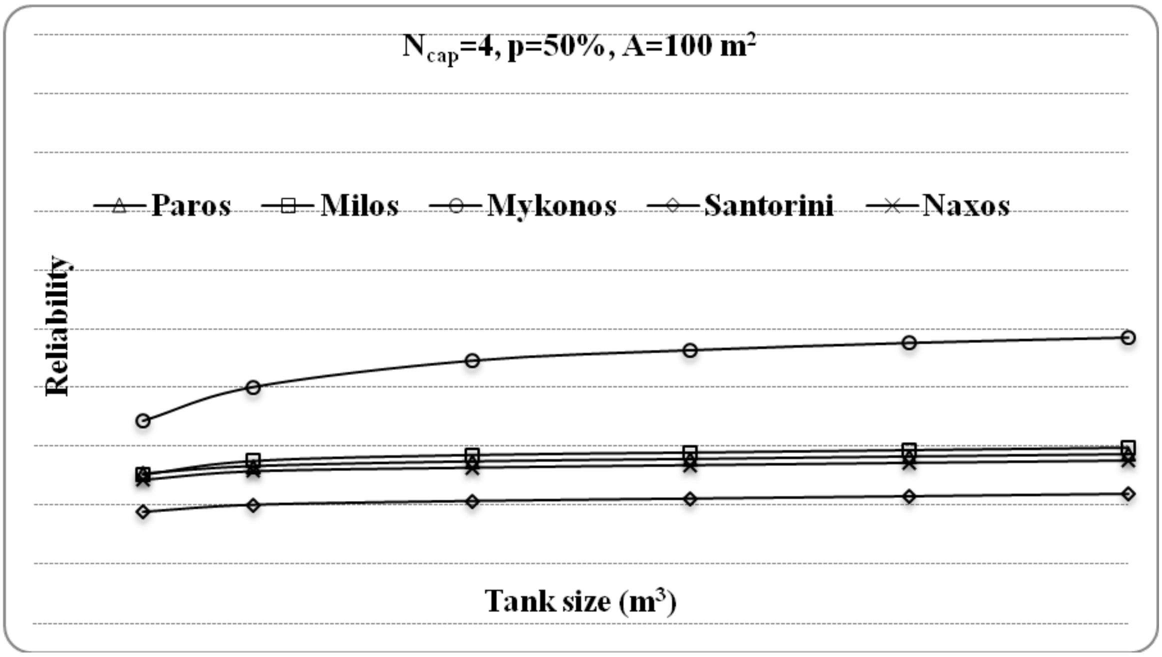


Figure 4. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 50% for 4-people household (300 L/day) with roof area of 100 m^2.

Figure 5 shows the reliability curves for high demand (300 L/day) - medium roof area (200 m^2) scenario. It is clear that by doubling roof area from 100 to 200 m^2 reliability increases with tank size but maximum value of 63% can be achieved only for 50 m^3 tank size for Mykonos island. Reliability ranges from 32% to 46% for tank size of 5 m^3 and 39% to 63% for tank size of 50 m^3. Among them Santorini has the lowest values due to the lowest rainfall (293 mm).

Finally, evaluating Fig. 6 which shows the high demand (300 L/day) - high roof area (300 m^2) scenario, it is observed that reliability increases with tank size and reaches higher values in all islands studied. Reliability ranges from 38% to 44% for tank size of 5 m^3, while with tank size of 50 m^3 reliability reaches values from 64 to 85%. Santorini still demonstrates the lowest reliability values.

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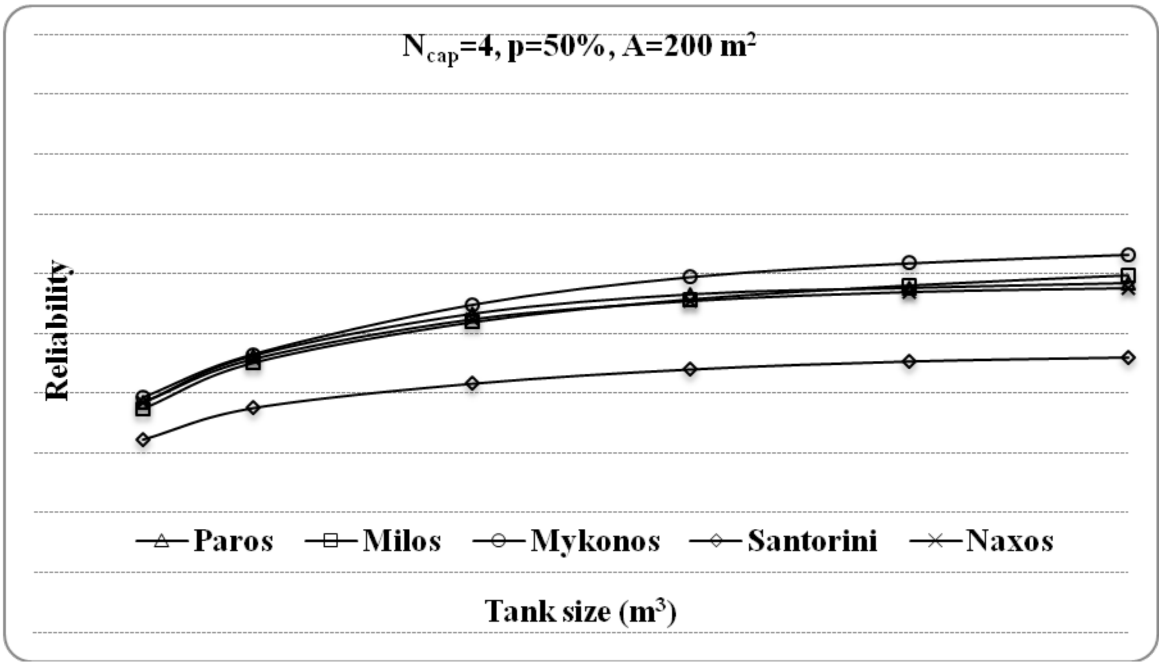


Figure 5. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 50% for 4-people household (300 L/day) with roof area of 200 m^2.

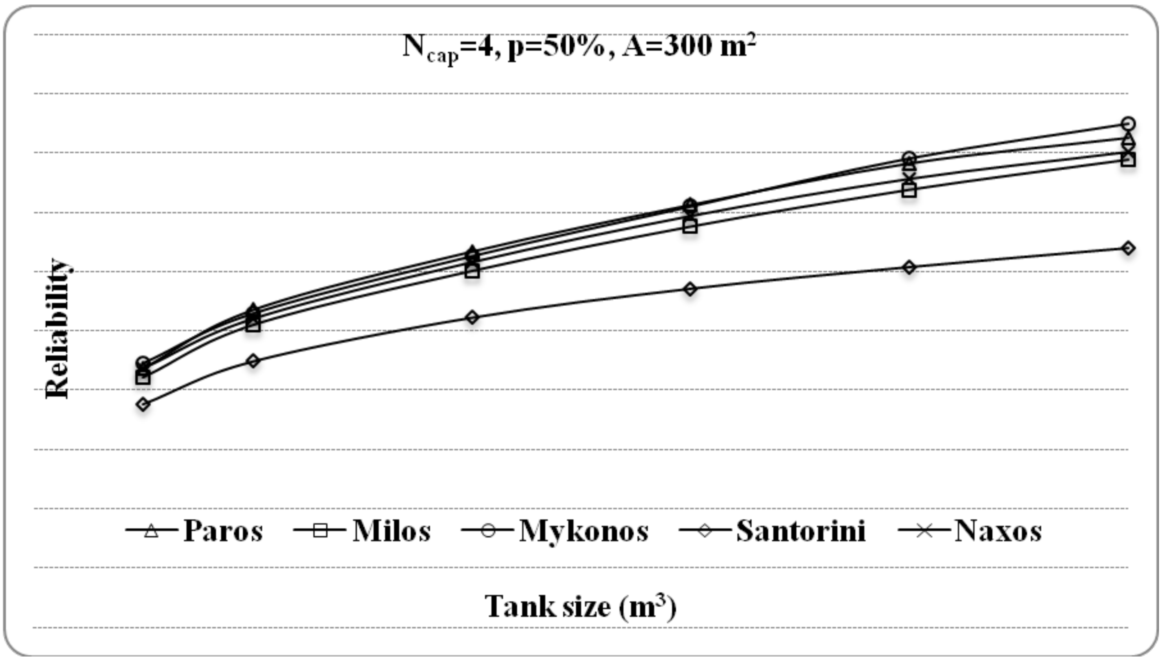


Figure 6. Reliability curves of rainwater harvesting system in relation to tank sizes to meet the demand of 50% for 4-people household (300 L/day) with roof area of 300 m^2.

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4. CONCLUSIONS

Reliability of rainwater harvesting tanks depends on several factors such as climatic conditions, roof area, tank size, household water demand and percentage of total water demand satisfied by harvested rainwater. The rainfall regime imposes the adoption of high tank sizes and roof areas in order to collect as much rain as possible. The roof area is the dominant limited factor which tank size cannot overcome. High reliability (> 80%) can be achieved for tank size greater than 20 m^3 for low water demand (135 L/day) and high roof area ($\geq$ 200 m^2). It is almost impossible to achieve 80% reliability in the case of high water demand (300 L/day) regardless of roof area and tank size. Among the five Cyclades islands studied, Mykonos presented the highest reliability values while Santorini the lower ones.

References

[1] Palla, A., Gnecco, I., Lanza, L.G., 2011. Non-dimensional design parameters and performance assessment of rainwater harvesting systems. *Journal of Hydrology*, **401**, 65-76.

[2] Ward, S., Memon, A., Butler, D., 2011. Rainwater harvesting: model-based design evaluation. *Water Science and Technology*, **61(1)**, 85-96.

[3] Campisano, A., Modica, C., 2012. Optimal sizing of storage tanks for domestic rainwater harvesting in Sicily. *Resources, Conservation and Recycling*, **63**, 9-16.

[4] Tsihrintzis, V., Baltas, E., 2014. Determination of rainwater harvesting tank size. *Global NEST Journal*, **16(5)**, 822-831.

[5] Londra, P.A., Theocharis, A.T., Baltas, E., Tsihrintzis, V.A., 2015a. Optimal sizing of rainwater harvesting tanks for domestic use in Greece. *Water Resources Management*, **29(12)**, 4357-4377.

[6] Ghisi, E., Tavares, D.F., Rocha, V.L., 2009. Rainwater harvesting in petrol stations in Brasília: potential for potable water savings and investment feasibility analysis. *Resources, Conservation and Recycling*, **54**, 79-85.

[7] Basinger, M., Montalto, F., Lall U., 2010. A rainwater harvesting system reliability model based on nonparametric stochastic rainfall generator. *Journal of Hydrology*, **392**, 105-118.

[8] Cowden, J.R., Watkins, Jr.D.W., Mihelcic, J.R., 2008. Stochastic rainfall modeling in West Africa: parsimonious approaches for domestic rainwater harvesting assessment. *Journal of Hydrology*, **361**, 64-77.

[9] Su, M., Lin, C., Chang, L., Kang, J., Lin, Mei., 2009. A probabilistic approach to rainwater harvesting systems design and evaluation. *Resources, Conservation and Recycling*, **53**, 393-399.

[10] Chang, N., Rivera, B.J., Wanielista, M.P., 2011. Optimal design for water conservation and energy savings using green roofs in a green building under mixed uncertainties. *Journal of Cleaner Production*, **19**, 1180-1188.

[11] Aladenola, O.O., Adeboye, O.B., 2010. Assessing the potential for rainwater harvesting. *Water Resources Management*, **24(10)**, 2129-2137.

[12] Eroksuz, E., Rahman, A., 2010. Rainwater tanks in multi-unit buildings: a case study for three Australian cities. *Resources, Conservation and Recycling*, **54**, 1449-52.

[13] Londra, P.A., Theocharis, A.T., Baltas, E., Tsihrintzis, V.A., 2015b. Effect of dry period on sizing of domestic rainwater harvesting tank. *Proceedings of 14th International Conference on Environmental Science and Technology* (ed. T.D. Lekkas), September 3-5, Rhodes, Greece.

[14] Yaziz, M.I., Gunting, H., Sapari, N., Ghazali, A.W., 1989. Variations in rainwater quality from roof catchments. *Water Research*, **23(6),** 761-765.

Exploiting energy recovery potential in a water distribution network along with reliable pressure management

M. Patelis*, I. Vasilopoulos, V. Kanakoudis, K. Gonelas

Department of Civil Engineering, University of Thessaly, Pedion Areos, Volos, GR 38334, Greece.
*Corresponding author: Email: patelis@uth.gr

Abstract

Water Distribution Systems (WDS) that operate gravitationally often present high nodal pressures. High pressure can have many negative effects to the network and its service, which leads water utilities to implement Pressure Management (PM) measures. This energy that is hidden inside a network and needs to be regulated and reduced, can be recovered instead. Hydro-turbines are widely used in small water energy production plants in order to turn water kinetic energy to electricity. PATs (Pumps as Turbines) are micro-turbines (turbines of small scale compared to the usual) used exactly in reverse to the usual pumps. Implementation of a PAT aims to produce energy along with managing to a desired level the pressure of the downstream pipe. PRVs (Pressure Reducing Valves) are used to decrease pressure aiming to reduce water losses. This study focuses on exploiting every possibility of replacing a PRV with a PAT and its ability to reduce pressure to acceptable levels as well as produce significant amount of energy. Water distribution system of Kozani city (in Northern Greece) is used as a case study. The various scenarios were implemented in network's calibrated hydraulic model with interesting results.

Keywords: PATs; PRVs; water loss

1. INTRODUCTION

Water kinetic energy has been taken advantage from mankind for many purposes throughout centuries. Most recent, water has unfolded a great opportunity for green energy production via turbines. Hydro-turbines are widely used in small water energy production plants in order to turn water kinetic energy to electricity. Pumps working as Turbines (PATs) are micro-turbines (small sized) working on "reverse mode" compared to the usual pumps. They are being installed to recover a significant part of the available kinetic/flow energy inside a pipe and convert this energy to electricity [1]. Produced electricity can be either high or low voltage (produced power usually varies from 1 to 200 KW). Water utilities in charge of either small or greater networks try to exploit this new opportunity in order to cover part of the energy needs of the Water Distribution Network (WDN) itself, or sell electricity to bring back revenue.

Although oil prices have decreased due to certain events in recent years, energy crisis is constant. Increased interest is shown into PATs as they are pumps that contribute to an energy self-sufficient network. Apart energy prices PATs contribute to environmental safety as they produce electricity from a renewable source. Although it is hard to detect and measure excessive energy and pressure potentials, after thorough studies and cross-checks, suitable places for energy production in WDSs can be spotted.

PATs are reliable producers of renewable energy [2]. Installation of a PAT in a water distribution network must comply with all its operational restraints. An additional great advantage of a PAT is its ability to reduce the downstream pressure, even close to zero. With certain modifications and operation patterns, some types of PATs are capable of maintaining a desired level of pressure control (such modifications have mechanical character and determine energy production as well as pressure

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management of a PAT but they do not consist research topic for this article). When a PAT is used also to control downstream pressure, energy produced is reduced, but benefits achieved are increased. Mechanical equipment and operation mode of a PAT, demand high dedication as a wrongly selected PAT can bring devastating results to the network's service levels and its energy production as well.

The best way to reduce Non-Revenue Water (NRW) level in a water distribution network has proven to be Pressure Management (PM). All PM strategies begin mainly by forming (dividing the network into several) District Metered Areas (DMAs) followed by Pressure Reducing Valves (PRVs) installation in several DMAs' entering points. An alternative to PRVs, are PATs that are used to perform Pressure Management as well as recover "green energy" from the water distribution network itself. This mechanical device has the same operational mode of a pump but instead of consuming energy to boost water, it takes advantage of water flow to produce electricity. As PATs operate similarly to other regular pumps, their implementation does not require many modifications to take place in the network. No specially trained personnel is needed to support and perform maintenance works related to PATs' operation. Additionally, spare parts for PATs are easy to find in the market. Purchase values and other implementation costs are quite low and in any case comparable to those of regular pumps. The only significant requirement is the existence of a naturally produced energy surplus. There have been many examples of PATs' implementation around the world during the last two decades [3], [4]. Still, the opportunity to recover energy from a water distribution network is not widely spread and adopted. Most of the PATs installation cases have taken place in the water supply mains of water distribution networks [5], where water is supplied in large diameter pipes from springs or drillings, sometimes covering long distances and starting from high altitudes. Except from a minimum of pressure and flow inside a pipe, the produced energy must have a purpose to exist. Energy production usually takes place near the energy consumption/demand site, otherwise power transmission network is required.

PATs unfold great opportunities [6], but thorough study is needed before equipment selection and installation. The complexity of the problem is high and it can easily turn such a promising investment into a failure. In order to implement PATs successfully, water utility managers need to cooperate with experienced researchers and equipment providers. An example of a PAT implementation project in the water distribution network of Kozani city (in Northern Greece) is presented as a case study in this paper.

2. CASE STUDY & METHODOLOGY

Kozani city, capital of Kozani County in West Macedonia Region, Greece, is located in the northern part of Aliakmonas river valley. The city lies 710 metres above sea level, 15 Km northwest of the artificial lake Polyfytos, 120 km south-west of the city of Thessaloniki (the second largest Greek city after Athens, the capital city), between Pieria, Vermio, Vourinos and Askio mountains. The population of Kozani municipality exceeds 70,000 people. The consumers being served by the local water utility (named DEYAK) are almost 50,000 people. Its well-designed water distribution network is widely spread covering a huge area (Figure 1), including the entire city and its expansions in more than ten suburbs. The total daily water volume supplied by the water distribution network reaches its peak (22,744m3) on July (a high figure that indicates great chance of high non-revenue water levels), while dropping to just 18,584m3 on January. Figure 2 presents the total water volumes (in a 4-months basis following the billing period adopted by DEYAK) produced (as produced is named the amount of water a water utility brings into the network to cover its needs) and consumed (measured) in Kozani in 2009 and 2010 [9]. Kozani during winter is being supplied by Ermakia springs (to the north), while during summer by Vathylakkos boreholes (to the south). There are three pressure zones formed: a) a limited higher (BLUE) zone at the north (altitude ranging from +750 to +800); b) a medium (RED) zone in the middle (altitude ranging from +710 to +750); and c) a low (GREEN) zone at the south (altitude ranging from +610 to +710), covering 60% of the total water demand (Figure 1). There are two main water storage tanks and also a tank system supplying only the middle zone [7].

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Figure 1. Kozani city WDN: (a) water tanks, pressure zones; (b) DMAs [7]

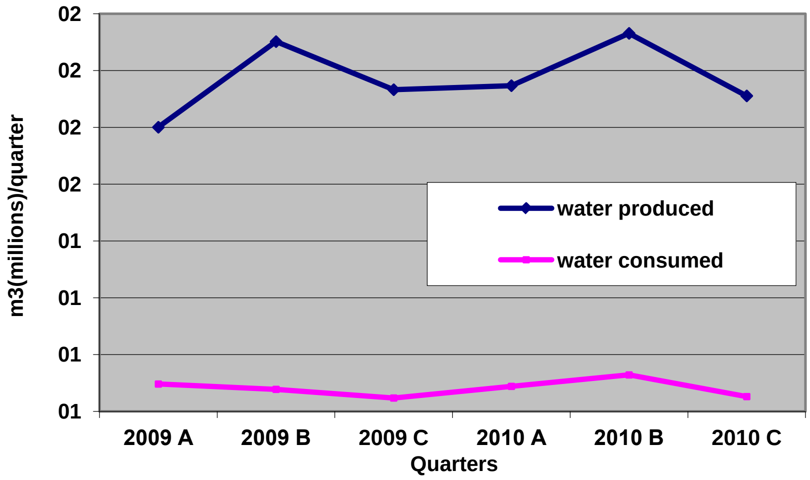


Figure 2. Water extracted (SIV) & consumed in the city of Kozani [7, 8]

The water distribution network of Kozani city was chosen for this study due to the high altitude difference observed in Kozani's topography. Thus, as already mentioned, the local (municipal) water utility (DEYAK) operates the network by supplying water into three pressure zones. The water distribution network has been further (virtually) divided into several DMAs through studies performed by the authors in the near past. Due to the high altitude difference observed, the network works sufficiently by gravity. There are nodes in the network where the available operating pressure gets as high as 10 atm, causing major problems to the network's operating status and life expectancy. Also water losses are increased and Non-Revenue Water (NRW) reaches 58% of the System's Input Volume (SIV) [8].

Virtual formation of the 24 DMAs took place using the network's hydraulic simulation model that was recently developed. The segmentation of the network was done by "installing" isolation valves in the pipes that define the DMAs' borders. Possible locations to install PATs were considered only the pipes supplying water to one or more DMAs. These "DMAs entrance pipes" were the only pipes checked as the aim of the study was twofold, thus not only to produce energy through PATs but also to

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reduce operating pressure like the Pressure Reducing Valves (PRVs) do, when installed in these DMAs entrance pipes. In order to test the implementation of a PAT, a pipe with excessive pressure potential must be pinpointed. All DMAs where included in this study despite their high complexity. Observation of some DMAs is far more complex due to the fact that although each DMA is being supplied by one pipe, the water may exit the DMA from one or more pipes (not all DMAs have one exit, some have more than one exit and supply several other DMAs). DMAs that provide water downstream (meaning that they are not the last downstream DMAs), affect other DMAs if upstream pressure is reduced. All DMAs' entrance pipes were selected as potential PAT installation positions. In order to determine a pipe's ability to produce power, equation 1 was selected to estimate the power of a hypothetically installed PAT. This equation has been used in the past from researchers for similar purposes [9,10] and is greatly used by many manufacturers to calculate energy production.

$$P_{el} = \Delta h * Q * g * \rho * n_{turb.} * n_{gen.} \quad (Watt) \tag{1}$$

$$P_{el} = m * m * m * kg = kg * m = J = W$$

P_{el}=power produced from turbine (Watt), Δh=Hydraulic Head difference (m), Q= water flow (m^3/s), g= acceleration of gravity (9,81 m/s^2), ρ= water density (1000 kg / m^3), $n_{turb.}$ = turbine efficiency factor (usually 0,8-0,9), $n_{gen.}$ = generator efficiency factor (usually 0,8-0,9)

Eighteen pipes were examined as potential PAT installation positions and their energy production was calculated according to equation 1. Only 11 were able to support a turbine of 2kW or more. 7 pipes were excluded as their flow and head difference were not enough to be exploited for energy production. According to what international market offers, suitable equipment was selected and implemented in each position. Each PAT was hydraulic simulated and tested on the WDN's hydraulic model. One great observation was that in some cases implementation of a PAT was able to control pressure in more than one DMA. As a result of the above, some PATs were neutralized because head difference and flow were decreased from a PAT implemented above them. In figure 3 there are pinpointed all seven turbines that were able to produce considerable energy.

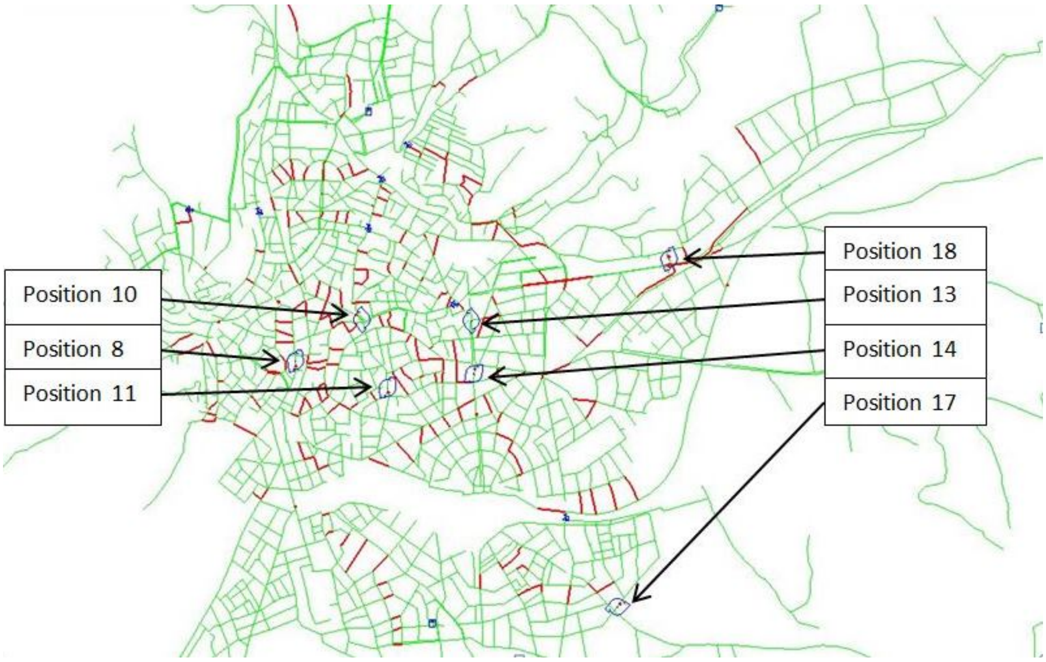


Figure 3. Positioning of PATs inside the WDN of Kozani city.

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In order to evaluate PATs as PM measure and not only as energy generators, their results were compared to those of PRVs. 3 scenarios were developed in this study, that all took place on the same seven DMAs selected above. In scenario No.1, the water distribution network is divided into DMAs, but no PRVs or PATs are installed. In scenario No.2, PRVs are placed in the entrance of each DMA. Each PRV is selected according to the diameter of the pipe and is regulated to operate on a steady initial pressure. Initial pressure of the PRV is maintained to the minimum level, where no node has pressure lower than 200 KPa (this minimum required nodal pressure is defined by the Greek legislation all water utilities obey). In scenario No.3, every PRV is replaced by a PAT. Pats are installed in exact same position where were the PRVs of scenario No.2. Each PAT has different power as shown in table 1. Turbine power is limited due to the restriction of minimum available nodal pressure (200 KPa) in every node of the DMA. Both types of PRV and PAT selected, have no daily pattern regulators, thus operate on a steady-state condition. Other guidelines defining the PAT type were market availability and cost.

Table 1. Power of each PAT in each position.

positions > 2 Kw		**PAT (KW)**
position 8	6.137108	5
position 10	12.37776	10
position 11	5.648943	4.5
position 13	6.679154	5
position 14	4.925985	4
position 17	4.0567	3
position 18	7.784024	6

All three scenarios were tested using the Bentley WaterGems v8. i software separately. The hydraulic model of Kozani city was firstly calibrated and validated in order to offer accurate results. After each scenario test, data was collected regarding reduction of DMAs' water input volume, annually recovered energy (in scenario No.3 only), equipment purchase cost, maintenance costs, worth of energy recovered and water volume being saved.

3. STUDY RESULTS

Each scenario resulted clearly after several tests in several advantages but also some disadvantages. Specifically, it can be observed that in scenario No. 2 there is better pressure management than in scenario No. 3. On the contrary only in the third scenario there is power production which can be used to cover several needs of the WDS and the water utility in charge. Reduction of SIV is a result of PM thus scenario No. 2 has greater reduction but No. 3 has reduced water volume significantly too. In table 2 there are details about scenario No. 1 were the initial state is explained. Table 3 describes how figures from first scenario developed, after PRV or PAT implementation.

Table 2. Pressure and flow in scenario No. 1.

	Pressure (Kpa)	Annual Average water Flow (L/s)	Annually saved water (cubic meters)	Annually recovered energy (kWh)
position 8 DMA 4K	588.26	28.73	0	0
position 10 DMA M	536.80	73.62	0	0
position 11 DMA 5	669.76	18.68	0	0
position 13 DMA 12	548.81	32.86	0	0
position 14 DMA 7	633.66	19.00	0	0
position 17 DMA K-2	710.39	13.58	0	0
position 18 DMA 18	644.62	30.71	0	0

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Pressure reduction in the second and third scenario was similar. In both scenarios PM was very efficient and reduction rates were from 34.50% to 62.94% for PRVs implementation and from 28.92% to 57.59% for PATs implementation. Difference in these two strategies was never above 9% compared to the initial state (scenario No.1). In terms of PM, scenario No.2 and No.3 are not identical but it can be understood that PATs do control pressure too. Pressure reduction rate is shown below in figure 4.

What is important for PM tactics apart from reduction of bursts and leaks, is reduction of Non-Revenue Water (NRW) as well as reduction of pressure dependent consumptions and other uses. All the above result into reduction of the system's input volume (SIV). Saving water is vital for recent water utilities as it is very hard to find new quality sources of water in many occasions. Annually saved water in scenario No.2 was different for every DMA but it summed up 2,238,318 cubic meters but scenario No.3 saved 405,000 cubic meters less. Energy production is also very important and gives PATs a major advantage. Only in the third scenario there is energy recovery from the network itself. Energy that otherwise would be wasted instead of used by the water utility in order to lower its operating costs, or produce revenue. Figure 4 depicts energy recovery and water saving of scenario 2 and 3 for each DMA separately.

Table 3. Pressure, flow, saved water, recovered energy. Row order is same as in Table 2.

PRV				PAT			
Pressure (Kpa)	Annual average Water Flow (L/s)	Annual water savings (m^3)	Annually recovered energy (kWh)	Pressure (Kpa)	Annual average Water Flow (L/s)	Annual water savings (m^3)	Annually recovered Energy (kWh)
277.08	22.06	210,244.87	0	316.24	23.46	166,009.7	43,800.0
324.61	55.84	560,469.56	0	345.18	59.04	459,654.4	87,600.0
248.19	12.60	191,688.47	0	284.02	13.46	164,376.2	39,420.0
359.46	24.07	277,240.82	0	390.11	26.56	198,799.7	43,800.0
250.90	13.12	185,197.00	0	328.73	15.11	122,505.4	35,040.0
310.60	10.23	105,550.35	0	316.51	10.32	102,613.5	26,280.0
340.11	8.26	707,926.62	0	391.16	11.08	618,989.8	52,560.0

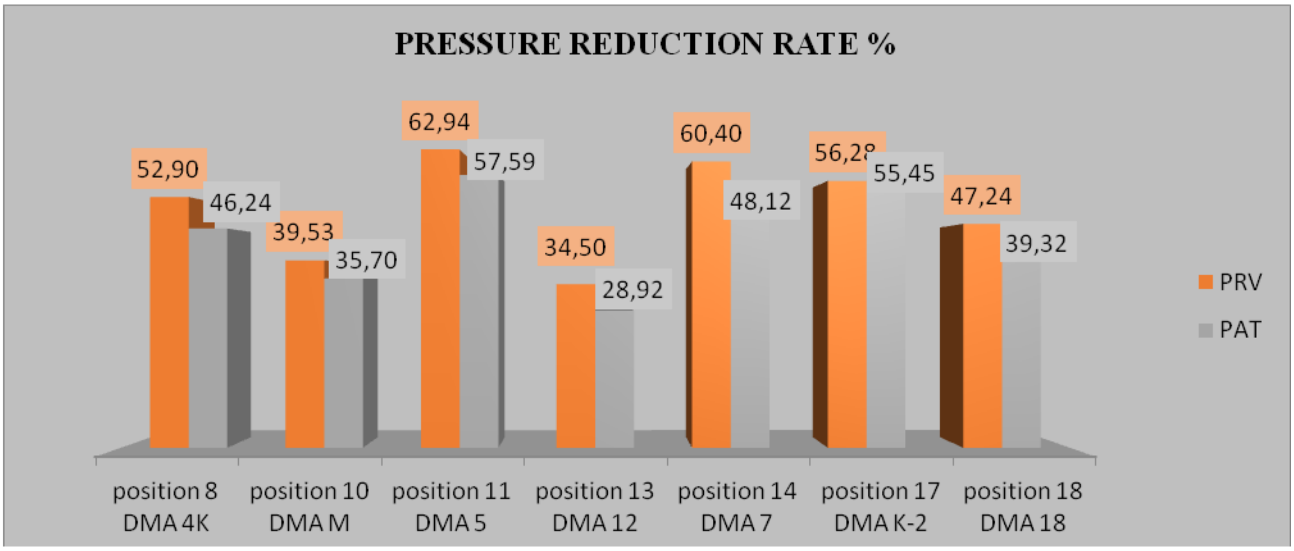


Figure 3. Pressure reduction rate of PRVs and PATs implementation.

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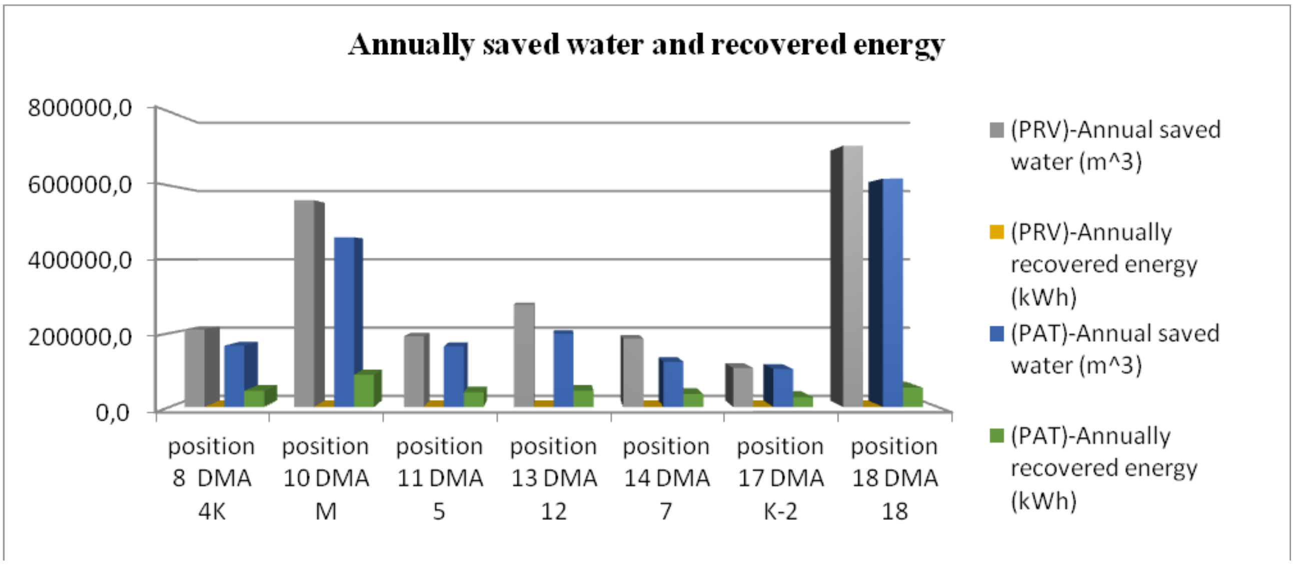


Figure 4. Annually saved water and recovered energy
(Numbers occur from hydraulic simulation of Kozani's city model)

Studying the results, it can be concluded that if applicable, PATs should be considered by water utilities as a valuable investment. Other than excessive energy, PATs should be implemented only when a need for energy is located near the recovery site. In any other case where no energy consumption can be satisfied nearby, PATs are not the optimal solution for pressure reduction as power transmission should take place. PRVs are more accurate and effective in reducing pressure and are easier to implement. Also equipment and maintenance cost differ for each scenario. Pats can be twice or more the price of PRVs and they require more advanced knowledge and personnel to monitor them. PATs implementation inside water distribution networks can take advantage of its dual benefit and prove to be the most valuable pressure management and energy recovery measure. Newer developed types of turbines make things more promising for PATs as recent models are capable of measuring downstream pressure and be self-modified to keep it at a certain level. Other improvements should take place in order to increase efficiency of mechanical equipment and limit other implementation risks. This way, the differences in pressure management compared to PRVs can be reduced and the energy recovery rate can be increased.

4. CONCLUSION

WDNs suffer from high pressure levels causing many problems as well as increasing SIV and NRW. DMAs implementation and PRVs installation are the most effective pressure management strategies up to recent years. PM tactics manage to reduce pressure along with all its negative effects but do not take advantage of water's surplus kinetic energy. PATs unfold a new opportunity for water distribution networks to recover energy but also perform effective pressure management. A properly implemented PAT can achieve significant energy production and DMAs' excessive pressure reduction. Combining PATs inside a water distribution network with bigger PATs in the water supply mains (before the main water tanks outside the city limits) can help a water utility to be self-sufficient in terms of energy needs. Pressure control is not as efficient as in the case of a PRV installation but figures do not pose great difference. Extra careful study must take place in order to define whether there is surplus energy in a network and find suitable positions for PATs' implementation. Unfortunately, not all water distribution networks are able to provide such locations. Efficient and cost-effective PATs require one major detail from the WDN. Water must

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flow inside only by gravity. Additionally, a need for energy consumption has to exist nearby the energy recovery site, otherwise energy must be transported for long distances or sold which might not be possible or expensive.

Three scenarios were tested in the current study to compare PRV and PAT implementation after the segmentation of a water distribution network in DMAs. Results for PRV installation were pretty much as expected, but PAT implementation did provide very promising results too. Out of the 24 DMAs in the water distribution of Kozani, 18 were selected in the case study as potential PAT implementation positions. Due to lack of excessive pressure and flow some of them were excluded, using an equation to calculate the potential power of a pipe. Finally, after hydraulic simulation, 7 positions were capable to produce power higher than 2kW and PATs were selected carefully in order to calculate pressure management too. Results were promising but not as good as PRVs in terms of PM. PATs can be very valuable providing dual benefits but need extra care and expertise in studying before implementation. Wrong selection of equipment, wrong positioning and calibration can have disastrous effects on the network. PRV and PAT implementation in every scenario should maintain the minimum pressure level requirements downstream in order to keep consumers satisfied. If further research is invested in PATs, then many problems regarding their efficiency or implementation could be solved.

References

[1] Paish O., 2002. Small Hydro Power: technology and current status. *Renewable and Sustainable Energy Reviews*, **6 (6)**, 537-556

[2] Jafari R., Khanjani M.J., Esmaeilian H. R., 2015. Pressure Management and Electric Power Production in Water Distribution System Using Pump as Turbine, *AWWA*, **107 (7)**, E351-E363 (in press)

[3] Williams A.A., 1996. Pumps as turbines for low cost micro hydro power, *Renewable Energy*, **9 (1-4)**, 1227-1234

[4] Williams A.A., Simpson R., 2009. Pico hydro-Reducing technical risks for rural electrification, *Renewable Energy*, 34 **(8),** 1986-1991

[5] Arriaga M., 2010. Pump as turbine-A pico-hydro alternative in Lao People's Democratic Republic, *Renewable Energy*, **35 (5)**, 1109-1115

[6] Agarwal T., 2012. Review of Pump as Turbine (PAT) for Micro-Hydropower, *International Journal of Emerging Technology and Advanced Engineering*, **2(11)**, 163-169

[7] Kanakoudis V., Gonelas K., Patelis M., 2014. Developing water pressure management scenarios to cut down the real losses in the water distribution system of Kozani, Greece, *Proceedings of the International Conference on Protection and Restoration of the Environment XII, June 29 – July 3*, Skiathos island, Greece, 248-255

[8] Kanakoudis V., Tsitsifli S., 2014. Verifying the usefulness of the IWA Water Balance 2nd modification: pinpointing the actual role of the fixed charge included in the water tariffs, *Proceedings of the International Conference on Protection and Restoration of the Environment XII, June 29 – July 3*, Skiathos island, Greece 240-247

[9] Bilal Abdullah Nasir 2013: "Design of Micro-Hydro-Electric Power Station ", *International Journal of Engineering and Advanced Technology* (IJEAT), ISSN: 2249 – 8958, Vol-2, Issue-5,pp.39-47

[10] Dilip Singh 2009: "Micro-hydro-power", *Resource Assessment Handbook, An Initiative of the Asian and Pacific Center for Transfer of Technology*

Wastewater Treatment and Management

PROTECTION AND RESTORATION OF THE ENVIRONMENT XIII

Domestic greywater treatment in a constructed wetland mesocosm planted with two species of macrophytes

A. Gupta*, R. Bhuyan

Department of Ecology & Environmental Science, Assam University, 788011, Assam, India
*Corresponding author: Email: abhik.eco@gmail.com

Abstract

Greywater or sullage is wastewater generated from households, commercial establishments and other sources that has not come into contact with faecal matter. In our study greywater from a household in a tea garden in Assam, India, was treated in a constructed wetland mesocosm which was designed as a scaled-down model of a vertical sub-surface flow (VSF) system planted with *Phragmites australis* or *Phragmites karka*. Variables such as electrical conductivity (EC), total dissolved solids (TDS), nitrate, phosphate, chloride and sulphate as well as trace elements such as Ca, Mg, Cd, Cr, Fe, Mn, Ni and Zn were reduced to varying extent after treatment with the two plant species. On the contrary, Cu and Pb concentrations were not reduced. The treated greywater could be reused for gardening or toilet flushing, thereby contributing towards recycling and conservation of water.

Keywords: greywater; constructed wetland; vertical sub-surface flow; heavy metals

1. INTRODUCTION

Wastewater treatment and recycling have become cherished objectives worldwide in view of the impending global water crisis. This crisis has already struck in many parts of the world, especially in the arid zones, and poses a stiff challenge to water managers, policy makers and all the stakeholders and end users alike. Wastewater is generally classified into two major types: 'black-' and 'grey-' water. The latter includes all wastewater generated from household activity except that from the toilet [1]. However, wastewater from kitchen is often classified separately as 'dark' water. Blackwater treatment and reuse involve sterilization and removal of pathogens and faecal matter, and consequently are far from easy tasks. Greywater, the treatment of which is less cumbersome, can be used for gardening, toilet flushing [2], and even in construction work for mixing concrete. However, greywater used in construction work must be low in impurities like chloride, sugar, salt, zinc. lead, calcium, oil, fat and detergents, since these can compromise the quality of concrete produced [3]. Such water can also corrode toilet plumbing and appliances if used for flushing. Similarly, greywater used for gardening or irrigation should have variables like pH, electrical conductivity (EC), total dissolved solids (TDS), nitrate, phosphate, chloride, hardness, sodium and toxic heavy metals such as cadmium, lead, zinc, chromium and others within permissible limits. Thus appropriate and adequate treatments of greywater are essential prerequisites for its safe and sustainable reuse and recycling. Water scarcity and poor water quality are among important concerns related to water resources management in water-stressed areas [4,5]. However, even in areas where water may be plentiful, greywater treatment and reuse can lead to improvement of natural water quality by reducing the pollution load [5]. This especially holds good for small towns and satellite townships in India and other developing countries where it is the practice to release

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untreated wastewater into receiving water bodies like rivers and lakes. In such areas, greywater treatment and reuse could be explored through the use of constructed wetlands (CWs).

Relatively few studies have been conducted in India on the efficacy of CWs [6-8]. Similarly, the suitability of employing CWs has been assessed in other developing countries such as Tanzania [9] and in the tsunami-affected areas of Thailand [10]. It has also been suggested that CWs could serve as stand-alone wastewater treatment systems in small villages [11]. The rich aquatic and semi-aquatic plant biodiversity of south and southeast Asia have remained relatively unexplored for their applied value in pollution biomonitoring and bioremediation. However, a few studies have revealed the phytoremediation potential of aquatic and semi-aquatic macrophytes that could be exploited for wastewater treatment [12,13]. A microcosm model has also been tested in an earlier study for treatment of laboratory greywater [2]. In view of the above, the present study aims to test a mesocosm model planted with two semi-aquatic macrophytes for domestic greywater treatment in Assam, India.

2. MATERIALS AND METHODS

2.1 Collection and acclimatization of experimental plants

Two species of semi-aquatic emergent macrophytes were used in the present experiment. These were: i) *Phragmites australis* Cav. Trin. Ex Steud; and ii) *Phragmites karka Trin. Fund.Ex Steud*. These were collected from wetland margins and marshy areas in and around the Assam University Campus at Dargakona, Cachar, Assam. The plants were brought to the laboratory and acclimatized for 15 days before the start of the experiment and placed in separate PVC containers filled with water for acclimatization.

2.2 Experimental Set Up for Greywater Treatment

For testing the waste treatment efficacies of the two macrophytes, an outdoor constructed wetland (CW) mesocosm was constructed in the West Jalinga Tea Estate, Cachar, Assam. This treatment system comprised a PVC tank which served as a storage-cum-sedimentation tank that first received the greywater generated from several households of the tea estate. From this tank, the greywater was fed into one of the three circular concrete tanks with a 16 L capacity. One of the tanks served as a control tank, having only gravel of 0.5-1 cm diameter. The other two tanks contained gravel beds planted with either *Phragmites australis* or *Phragmites karka* (Fig. 1). The effluent greywater after retention in these tanks was collected for analysis from the bottom of the tank which was fitted with an outlet with a stopcock. Thus these mesocosms served as miniature Vertical Sub-Surface Flow (VSSF) constructed wetlands. Each mesocosm was planted with a single species of macrophyte. After each experiment the mesocosms were thoroughly drained and flushed with tap water.

2.3 Sample Collection

Grey water samples were collected before it was subjected to any treatment. Water samples were also collected from the bottom outlet at the Hydraulic Retention Time (HRT) interval of 30 h. Thus the water samples collected belonged to either of the following categories: i) untreated greywater (Raw); ii) greywater from the control microcosm containing only gravel at 30 h HRT (Control); and iii) greywater after being treated in mesocosm planted with *P. australis* or *P. karka* at 30 h HRT. The experiment was repeated thrice with three replicate samples collected in the first two and two replicates in the third experiment.

2.4 Water Analysis

Wastewater samples were collected before and after a treatment time of 30 hours in clean PVC bottles and divided into two parts. One part was analysed for pH, electrical conductivity (EC), total dissolved solids (TDS), total alkalinity (TA), phosphate, nitrate, total hardness, chloride and sulpha-

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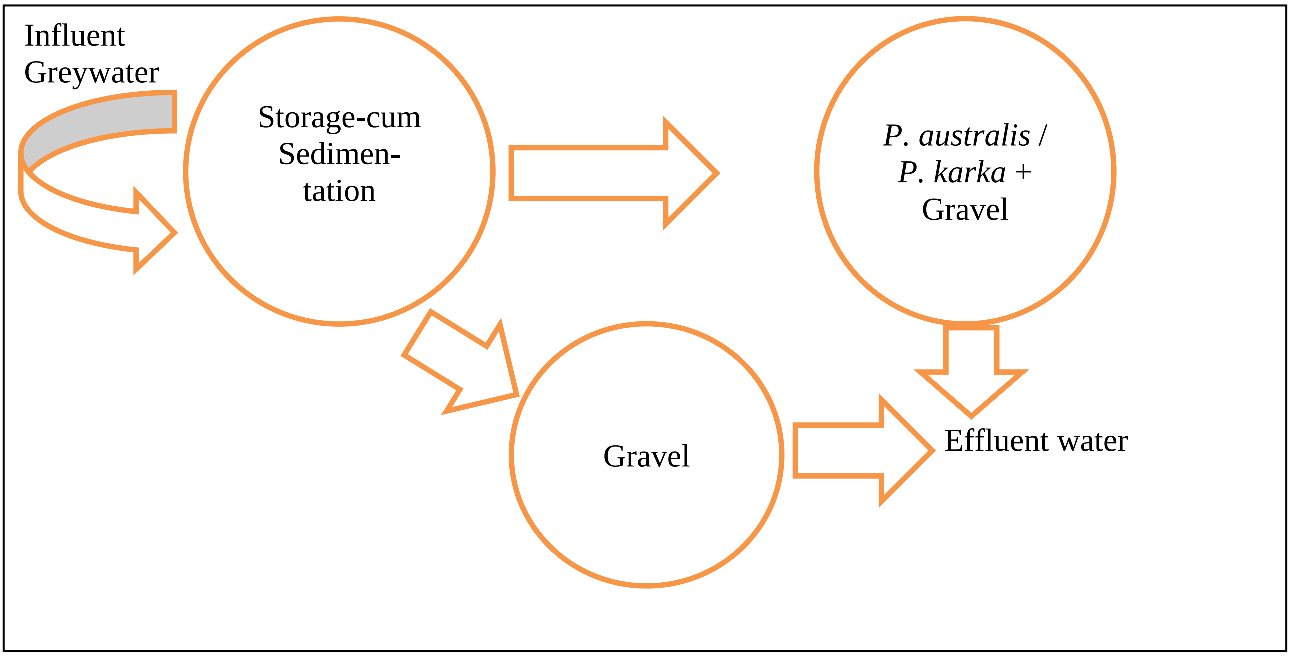


Figure 1. Schematic representation of the greywater treatment set up at West Jalinga Tea Estate, Cachar, Assam.

sulphate using standard methods [14, 15]. Sodium content in the samples was determined with a flame photometer (Systronics India). The other part was acidified with concentrated HCl (1 ml L^{-1}) and trace elements and heavy metals such as Ca, Mg, Fe, Mn, Cd, Cr, Cu, Pb, Ni and Zn were estimated by graphite furnace atomic absorption spectrometry (Analytik Jena Vario – 6). Metal contents in water samples were analyzed following previous studies [16].

3. RESULTS AND DISCUSSION

3.1 Physico-chemical properties of greywater before and after treatment

The physico-chemical properties of the influent domestic greywater before treatment and after passing it through only gravel bed or through gravel beds planted with either *Phragmites australis* or *Phragmites karka* for a hydraulic retention time (HRT) of 30 hours are shown in Table 1. As shown in the Table, the mean pH of influent domestic greywater was slightly acidic, and it was neutralized to some extent in gravel, *P. australis* and *P. karka* with the latter having the highest efficiency and gravel the least. Both EC and TDS were reduced more efficiently by *P. karka*, which was also most effective in reducing nitrate and sulphate and augmenting total alkalinity. *P. australis* most effectively reduced phosphate, chloride and sodium. Treatment through only gravel resulted in the least improvement of greywater quality. On the contrary, concentrations of some variables such as nitrate, sulphate and sodium were increased and alkalinity reduced in gravel treatment. The range of values of the variables revealed that there were high variations in several variables, indicating that the physico-chemical properties of domestic greywater could fluctuate greatly because of the wide range of impurities entering the domestic greywater from laundry, kitchen and bathroom. For instance, although the mean pH of influent greywater was a safe 6.32, the lower and upper extremities could be 4.24 and 9.57, respectively, suggesting that while on the one hand, acidic materials like vinegar, lemon juice and peels could lower the pH, preponderance of alkaline materials such as baking soda and others could push it to the other extreme. It can also be seen that both *P. australis* and *P. karka* could effectively moderate and keep the pH within acceptable limits.

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Comparisons with the Indian Standards for irrigation water quality as laid down by the Bureau of Indian Standards (URL-1) [17] reveal that while the values of EC, TDS, chloride and sodium in untreated influent water could sometimes go beyond the desirable or even permissible limits, treatment with *P. australis* and *P. karka* could bring these down to safe limits. The concentrations of all heavy metals remained well within the desirable limits, and they did not pose any problem for irrigation or concrete mixing [3]. Sodium and EC levels in greywater after treatment in constructed wetland mesocosms could be considered as belonging to the "Good" category [17].

Table 1. Physico-chemical properties of greywater before and after treatment with only gravel, *Phragmites australis* and *Phragmites karka* with a hydraulic retention time of 30 hours

	Mean ± S.E. (Range)			
Variables	**Influent**	**Gravel**	***P.australis***	***P. karka***
pH	6.32 ± 0.62 (4.24-9.57)	6.47 ± 0.31 (4.82-7.12)	6.73 ± 0.2 (5.73-7.36)	6.82 ± 0.22 (5.5-7.36)
EC (mS cm^{-1})	0.65 ± 0.28 (0.13-2.46)	0.47 ± 0.08 (0.25-0.95)	0.46 ± 0.04 (0.26-0.58)	0.38 ± 0.04 (0.17-0.51)
TDS (ppt)	0.42 ± 0.19 (0.09-1.63)	0.31 ± 0.05 (0.16-0.62)	0.3 ± 0.03 (0.17-0.36)	0.25± 0.03 (0.12-0.33)
Nitrate mg L^{-1}	0.31 ± 0.05 (0.17-0.43)	0.41 ± 0.26 (0.09-1.17)	0.17 ± 0.17 (BDL-0.84)	0.1 ± 0.03 (BDL-0.17)
Phosphate mg L^{-1}	16.84 ± 5.55 (0.88-47.13)	15.37 ± 4.85 (0.88-32.75)	1.63 ± 0.31 (0.75-2.5)	11.07 ± 3.67 (2.38-27.5)
Alkalinity mg L^{-1}	161.62 ± 53 (39.04-456)	130.18 ± 23.15 (68-256)	148.23 ± 21.85 (39.04-244)	192.06 ± 17.5 (92-244)
Total hardness mg L^{-1}	4.18 ± 0.08 (4.04-4.26)	4.03 ± 0.35 (3.48-4.4)	4.1 ± 0.05 (4.06-4.19)	4.07 ± 0.01 (4.07-4.08)
Chloride mg L^{-1}	106.7 ± 52.66 (25.99-459.8)	58.47 ± 16.89 (11.99-159.92)	41.73 ± 10.56 (6-75.96)	49.98 ± 9.87 (15.99-87.98)
Sulphate mg L^{-1}	32.41 ± 8.42 (8.95-74)	45.15 ± 10.55 (5.97-88)	14.0 ± 1.58 (8.95-18.64)	11.82 ± 3.03 (2.98-25.35)
Sodium mg L^{-1}	80.03 ± 4.11 (72.92-87.14)	82.52 ± 1.4 (80.09-84.94)	20.21 ± 8.79 (5-35.42)	21.89 ± 9.76 (5-38.77)

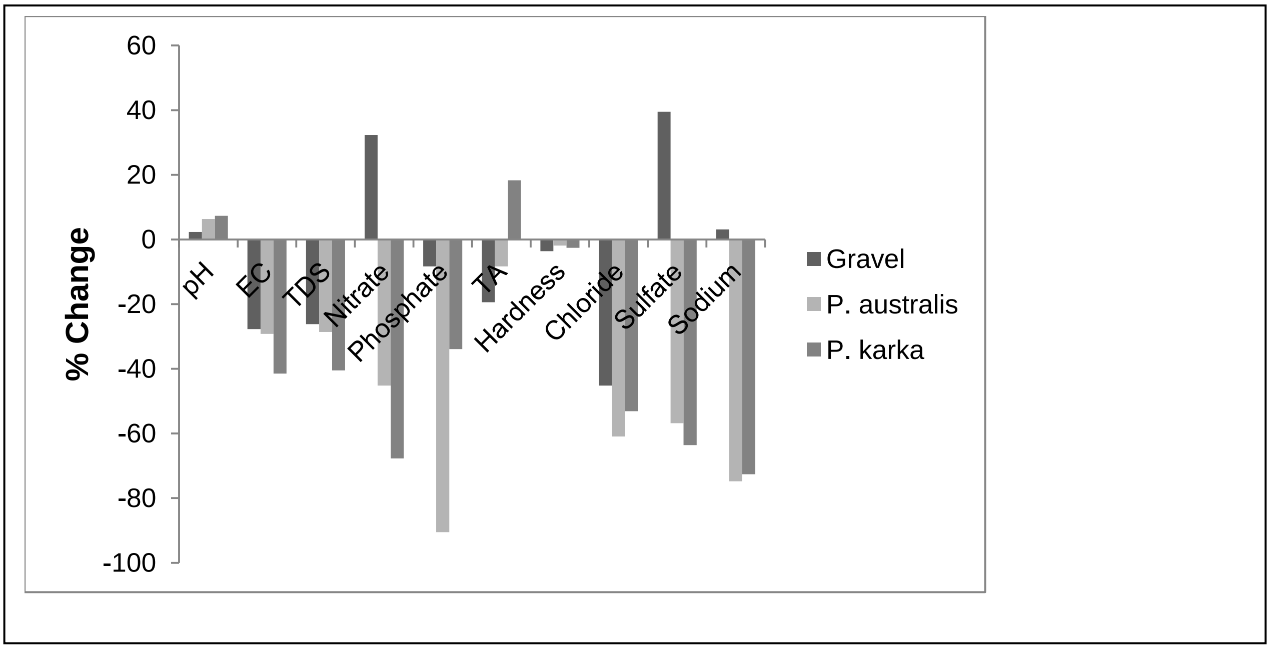
BDL: Below detection limit; EC: Electrical conductivity; TDS: Total dissolved solids

The percentage reduction or increase in the different physico-chemical variables from that of the untreated influent greywater under the three treatments is shown in Figure 2.

3.2 Removal of heavy metals in constructed wetland mesocosms

The concentrations of nutrients like Ca and Mg and some heavy metals in the influent greywater and after treatment in gravel bed and with *P. australis* and *P. karka* are given in Table 2. The concentrations of Cu, Fe, Mg and Ni were relatively high in the influent greywater, while the rest of the metals were well within safe limits. It is also seen that Cu could not be reduced appreciably by either of the macrophytes, while its concentration increased in gravel treatment. However, Cu at these concentrations is not likely to be toxic and instead may act as a micronutrient for plants. Fe and Ni concentrations were relatively high in the greywater of the tea garden, although both could be removed by treatment. Since the treated greywater has low chloride, sulphate, and metals like Ca, Zn and others, it can be easily used for mixing with concrete (Peche et al.)[3], as well as for other purposes such as irrigation of tea bushes and other plants, or for toilet flushing.

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EC: Electrical conductivity; TDS: Total dissolved solids; TA: Total alkalinity

Figure 2. Percentage changes in physico-chemical variables in the three different treatments from that of the untreated influent greywater
Gravel: Only gravel; P. australis: *P. australis* bed + gravel; P. karka: *P. karka* bed + gravel

It can be observed from Figure 2 that reductions in phosphate, chloride, sulphate and sodium were the most pronounced, being over 50 %.

3.2 Removal of heavy metals in constructed wetland mesocosms

The concentrations of nutrients like Ca and Mg and some heavy metals in the influent greywater and after treatment in gravel bed and with *P. australis* and *P. karka* are given in Table 2. The concentrations of Cu, Fe, Mg and Ni were relatively high in the influent greywater, while the rest of the metals were well within safe limits. It is also seen that Cu could not be reduced appreciably by either of the macrophytes, while its concentration increased in gravel treatment. However, Cu at these concentrations is not likely to be toxic and instead may act as a micronutrient for plants. Fe and Ni concentrations were relatively high in the greywater of the tea garden, although both could be removed by treatment. Since the treated greywater has low chloride, sulphate, and metals like Ca, Zn and others, it can be easily used for mixing with concrete (Peche et al.)[3], as well as for other purposes such as irrigation of tea bushes and other plants, or for toilet flushing.

The percentage reduction of elemental concentrations after treatment with only gravel and with *P. australis* or *P. karka* is shown in Figure 3. Cu reduction is very less in *P. australis* treatment, while its concentration increases marginally in *P. karka* and substantially in gravel bed. Cd reduction is also only 2 % in *P. karka* treatment, while there is increase in gravel as well as *P. australis* treatment. However, Cr is effectively reduced in all the three treatments in the range of 51-52 %. Ca reduction is moderate (about 11-15 %) in *P. australis* and *P. karka* treatments. *P. australis* was the most efficient in Fe removal, followed by *P. karka*. On the contrary, Mn removal was the highest in *P. karka*, followed by *P. australis*. Pb removal was only observed in *P. australis*, while Ni and Zn concentrations were reduced in all the three treatments, with the highest Ni removal in *P. australis*, and Zn in *P. karka*.

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Table 2. Trace element concentrations in greywater before and after treatment with only gravel, *Phragmites australis* and *Phragmites karka* with a hydraulic retention time of 30 hours

	Mean ± S.E (Range)			
Concentration μg L^{-1}	**Influent**	**Gravel**	***P. australis***	***P. karka***
Cu	452 ± 60.96	726.5 ± 169.67	431.56 ± 41.98	454.25 ± 60.72
Cd	6.63 ± 1.51	8.74 ± 2.68	8.43 ± 3.11	6.5 ± 2.6
Cr	8.83 ± 1.94	4.25 ± 0.75	4.23 ± 0.92	4.2 ± 0.08
Ca	71.25 ± 8.39	72 ± 1.08	63.25 ± 7.18	60.25 ± 9.5
Mg	971 ± 12.3	941.25 ± 45.54	956.75 ± 11.75	945 ± 0
Fe	2295 ± 222.84	1967 ± 341.05	1723.2 ± 159.13	1905.75 ± 249.24
Mn	33.88 ± 8.73	28.53 ± 11.71	23.56 ± 5.23	18.25 ± 3.75
Pb	7.55 ± 2.3	19.96 ± 11.35	6.78 ± 1.71	9.43 ± 2.36
Ni	314.25 ± 34.1	208 ± 33.81	144.94 ± 21.1	205.75 ± 16.56
Zn	9.68 ± 1.2	6.23 ± 1.03	4.93 ± 1.37	4.5 ± 1.19

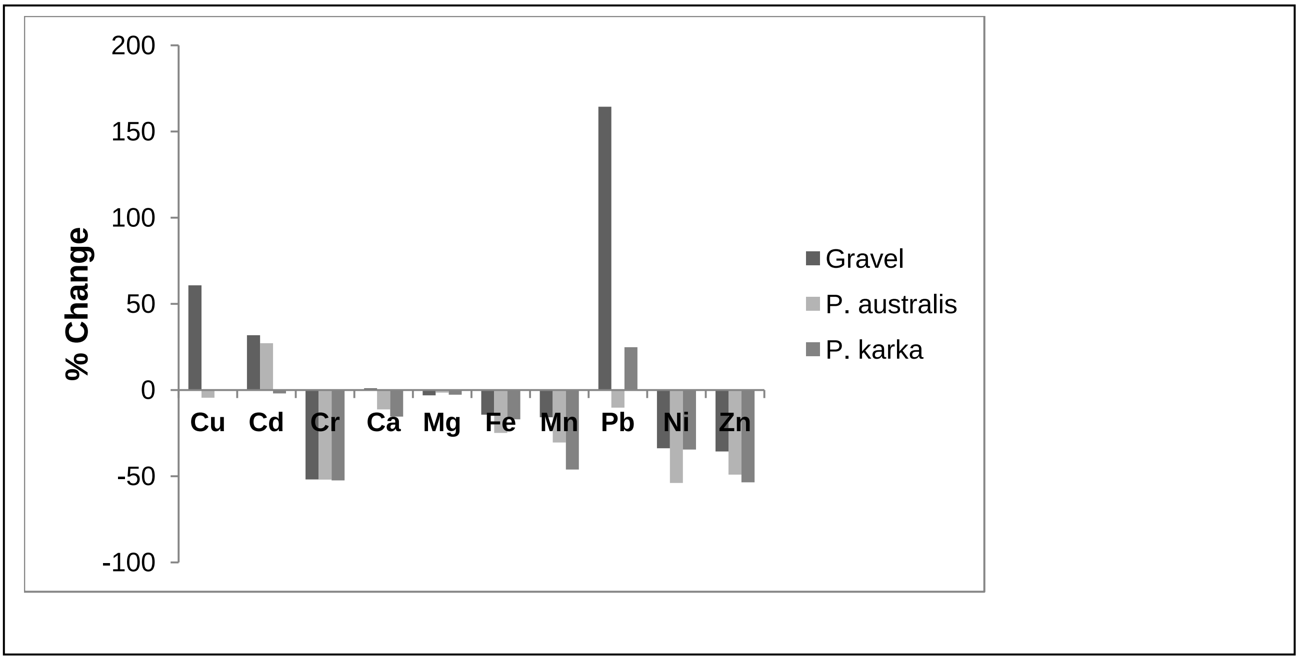


Figure 3. Percentage changes in elemental concentrations in the three different treatments from that of the untreated influent greywater
Gravel: Only gravel; P. australis: *P. australis* bed + gravel; P. karka: *P. karka* bed + gravel

Greywater treatment and reuse are gaining importance in many low and middle income countries, where inadequate wastewater treatment is having adverse impact on both public and environmental health. Also, greywater in water-stressed countries might be viewed as an important resource that could contribute towards the mitigation of water scarcity [2,5]. An overview of the different

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greywater management systems installed in several developing countries such as Mali, South Africa, Costa Rica, Nepal, Jordan and others were made [5]. The study reveals that greywater management offers innovative approaches often combining grease-and-grit traps and filters with horizontal and vertical flow constructed wetlands. The treated water is used for irrigating fruit and vegetable plots or fed into fish ponds. The results obtained in the present study suggest that the use of native or naturalized aquatic or semi-aquatic macrophytes in tandem with sedimentation chambers and septic tanks could be further explored to standardize these systems and popularize them in priority areas.

4. CONCLUSIONS

The present study analysed the physico-chemical properties of domestic greywater generated in a tea estate in North East India and the changes that occurred after this water was treated in vertical sub-surface flow constructed wetland mesocosms having gravel beds planted with *Phragmites australis* and *Phragmites karka*. The results obtained suggest that while *P. australis* was more efficient in reducing phosphate and chloride, *P. karka* neutralized pH and reduced the concentrations of EC, TDS, nitrate and sulphate more effectively. Among the heavy metals investigated, *P. australis* was more efficient in removing Ni, while *P. karka* removed Zn and Mn to greater extents. However, these plants were not very effective in removing or reducing the concentrations of Cd, Cu and Pb. Thus more aquatic and semi-aquatic plants need to be screened in a constructed wetland set up for evaluating their efficacies in moderating different physico-chemical variables as well as xenobiotics such as heavy metals and pesticides to create a local / regional database that could be used in combinations appropriate for a given situation. For instance, it has been shown that *Ipomoea aquatica*, a semi-aquatic macrophyte, could hyperaccumulate Cu and could effectively remove it from contaminated medium [12], while *Alternanthera philoxeroides* could accumulate and remove Cd from municipal wastewater [13]. The rich plant biodiversity of North East India, which is a part of the Indo-Burma Biodiversity Hotspot deserves special attention while creating this database. At the same time, regulations mandating separation of blackwater and greywater need to be incorporated into the building standards of urban areas. Builders and promoters in urban centres and the general population in cities, small townships and rural areas alike need to be made aware of the immense possibilities of treating and reusing greywater for improving sanitation and natural water quality and for addressing water scarcity.

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References

[1] Noah, M., 2002. Graywater use still a gray area. *Journal of Environmental Health*, **64**, 22-25.

[2] Gupta, A., Barman, M., Naiding, S., 2015. Laboratory greywater treatment in a constructed wetland microcosm using aquatic macrophytes. In: *Reviving Traditional Water & Environment Conservation Techniques: Proceedings of the IX World Aqua Congress* (ed. S. Rana), November 26-27, New Delhi, India, 116-126.

[3] Peche, R.T., Jamkar, S.S., Sadgir, P.S., 2014. Grey water – a potential source of water for construction. *IOSR Journal of Mechanical and Civil Engineering*, 12-17.

[4] UNESCO, 2003. Water for People, Water for Life. World Water Assessment Programme. The United Nations World Water Development Report, 92-3-103881-8.

[5] Morel, A., Diener, S. 2006. Greywater Management in Low and Middle-income Countries. SANDEC Report No. 14/06. SANDEC (Department of Water and Sanitation in Developing Countries) at Eawag (Swiss Federal Institute of Aquatic Science and Technology), Dübendorf, Switzerland.

[6] Vipat, V., Singh, U.R., Billore, S.K., 2008. Efficacy of rootzone technology for treatment of domestic wastewater: Field scale study of a pilot project in Bhopal (M.P), India. *Proceedings of Taal 2007: The 12th World Lake Conference* (eds. Sengupta, M. and Dalwani, R.), Jaipur, India, 995-1003.

[7] Yadav, A.K., Kumar, N., Sreekrishnan, T.R., Satya, S. and Bishnoi, N.R. 2010. Removal of chromium and nickel from aqueous solution in constructed wetland: Mass balance, adsorption-desorption and FTIR study. *Chemical Engineering Journal*, **160**, 122-128.

[8] Yadav, A.K., Jena, S., Acharya, B.C. and Mishra, B.K. 2012. Removal of azo dye in innovative constructed wetlands: Influence of iron scrap and sulfate reducing bacterial enrichment. *Ecological Engineering*, **49**, 53-58.

[9] Kaseva, M.E., 2004. Performance of a sub-surface flow flow constructed wetland in polishing pre-treated wastewater – a tropical case study. *Water Research*, **38**, 681-687.

[10] Brix, H., Koottatep, T., Laugesen, C. H., 2007. Wastewater treatment in tsunami affected areas of Thailand by constructed wetlands. *Water Science & Technology*, **56(3)**, 69-74.

[11] Solano, M.L., Soriano, P., Ciria, M.P., 2004. Constructed wetlands as a sustainable solution for wastewater treatment in small villages. *Biosystems Engineering* **87 (1)**, 109-118.

[12] Chanu, H.K. and Gupta, A., 2014. Necrosis as an adaptive response to copper toxicity in *Ipomoea aquatica* Forsk. and its possible application in phytoremediation. *Acta Physiologiae Plantarum* **36**, 3275-3281.

[13] Nimisha, Gupta, A., 2015. Uptake and accumulation of Cd from wastewater by *Alternanthera philoxeroides* (Mart.) Griseb. *Indian Journal of Applied Research* **5 (5)**, 19-20.

[14] Michael, P., 1984. Ecological Methods for Field and Laboratory Investigations. Tata McGraw-Hill Publishing Company Ltd., New Delhi, India, 454 pp.

[15] Rice, E.W., Baird, R.B., Eaton, A.D., Clesceri. L.S., 2012. Standard Methods for the Examination of Water and Wastewater, 22nd Edition. American Public Health Association, Washington, D.C.

[16] Gupta, A., 1996. Heavy Metals in Water, Periphytonic Algae, Detritus, and Insects from Two Streams in Shillong, Northeastern India. *Environmental Monitoring and Assessment* **40**, 215-223.

[17] URL-1. http://wqaa.gov.in/WriteReadData/UserFiles/Documents/WaterQualityStandards.pdf [Downloaded on May 01, 2016].

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Investigation of the biodegradation of Ibuprofen (IBU) residues by using an Extended-Aeration Activated Sludge Process

M. Maaroof[1], Y. Uysal[2*]

[1] Department of Environmental Engineering, Selcuk University, 42030, Konya, Turkey.
[2] Dept. of Environmental Engineering, Faculty of Engineering and Architecture, Kahramanmaras Sutcu Imam University, 46100, Kahramanmaras, Turkey.
*Corresponding author: Email: yagmuruysal@gmail.com

Abstract

Pharmaceuticals are continually being introduced to municipal wastewater treatment plants, and they have potential to affect the efficiency of the biological wastewater treatment processes. Thus, it is critical to observe these pharmaceuticals for biodegradation on the activated sludge. Ibuprofen is a non-steroidal acidic anti-inflammatory drug that is largely used throughout the world. In this study, the removal efficiency of Ibuprofen with aerobic biodegradation was investigated in a laboratory-scale Extended-Aeration Activated Sludge Process (EASP). Five batch bioreactors were operated at different hydraulic retention times of 12-52 h, and Ibuprofen concentrations of 0.01-10 mg/L. It was determined that aerobic biodegradation is dominant removal mechanism of IBU. The maximum removal efficiencies of IBU of 0.01 mg/L were obtained as 77.9%, 85.0%, 94.7% and 99.9%, for different HRT values of 12, 24, 36 and 52h, respectively.

Keywords: activated sludge; biodegradation; ibuprofen; removal; wastewater

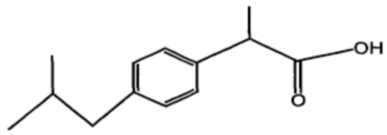
1. INTRODUCTION

The activated sludge process is a suspended – culture system that has been in use since the early 1900s. The process derives its name from the fact that settled sludge containing living, or active, microorganisms is returned to the reactor to increase the available biomass and speed up the reactions. It may be either a completely mixed or plug flow process [1, 2]. The extended aeration activated sludge process used in this study is a modification of the activated sludge process in which aeration time is increased to about 18-24 h, and has high mixed liquor suspended solids between 3500-5500 mg/L [3]. Ibuprofen 2-(4-isobutylphenyl) was derived from propionic acid by researchers at the Boots Company (Boots Group Plc, UK) during the 1960s. Ibuprofen (IBU) is commonly used for the relief of symptoms of arthritis, fever, primary menstrual pains. It is non-steroidal anti-inflammatory drug (NSAID) and analgesic that reducing pain without loss of consciousness [4]. IBU is present on the market in a number of products in which it is either the only active substance or in combination with the other active ingredients or percipients (Table 1). Excretion of ibuprofen takes place almost completely via the urine. The World Health Organization (WHO) includes ibuprofen in its "Essential Drugs List" of minimal medical needs for a basic health care system [5]. The therapeutic dose of the drug is large (up to 1200 mg/d) and 70-80% of this is voided un-metabolized after use. Therefore, large proportion of ibuprofen is reaching to Wastewater Treatment Plants (WWTPs) with domestic wastewater. For example, the compound has been detected in Finnish surface water in concentrations up to 65ng/L, and in WWTP influents and effluents of 20μg/L and 4μg/L, respectively [6]. Many studies have shown that ibuprofen does not volatilize or sorbs to the sludge. The only main removal method of ibuprofen is therefore

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biodegradation. The drug oxidizes to hydroxyl and carboxyl metabolites in WWTPs, and this often contributes to the high removal rates. Most of the drug biodegrades in the aeration tank during secondary treatment in a conventional WWTP with activated sludge. The total removal of ibuprofen in WWTPs can be up to 97% [6]. In spite of the fact that the drug has a high removal rate in activated sludge, it is still detected in environmental waters due to the high influent level [7,8,9]. It was discovered that ibuprofen was not degraded by the ammonia-oxidizing bacteria *Nitrosomonas europaea*, but it did degrade in nitrifying activated sludge. On the other hand, some studies have detected ibuprofen-degrading bacteria in WWTPs [13].

Table 1: The most properties of Ibuprofen (a. [10]; b. [11]; c. [6]; d. [12]; e. [7].

INCI Name	Ibuprofen		
Chemical Name	Benzeneacetic Acid, alpha-Methyl-4-(2-Methylpropyl)-		
Scientific name	a-Methyl-4-[isobutyl] phenyl acetic acid		
Trade Names	Advil, Children's Advil/Motrin, Medipren, Motrin, Nuprin, Pedia Care Fever.		
Molecular Formula	$C_{13}H_{18}O_2$		
Molecular Weight	206.28082 g/mole		
Biodegradation K_{biol}	21-35 [a]	23 ± 10 [b]	6.8 ± 3.3 [c]
Sorption coefficient log k_d	0.007 ± 0.002 [a]	0.9-1.4 [d]	
Sorption potential log k_{ow}	3.97 [e]	3.5-4.5 [d]	3.5 [b]
Physical form	Colorless, crystalline stable solid		
Chemical structure			

In a laboratory experiment carried out at 17 ± 1°C temperature, wastewater taken from a WWTP was spiked to certain levels of ibuprofen, and the biodegradation of the compound was tested in a batch system with MLSS concentration of 3.2g/L. The sludge used in the experiment had a sludge age of 11 ± 1 days, and COD concentration of the influent wastewater was 275mg/L. The reaction rate constant described as k_{biol} concerning their removal value were found as 21-35 L/gSS/d [10]. This value shows that Ibuprofen is highly biodegradable compound. The present study was aimed to investigate treatment performance of an laboratory scale EASP to remove IBU from wastewater.

2. MATERIALS AND METHODS

2.1. Activated Sludge Samples

In the experiments, five aerobic batch bioreactors set in the laboratory were operated. The activated sludge samples were taken from the Gaziantep municipal WWTP, and inoculated to the bioreactors with volume of 5 L. The bioreactors were built from Plexiglas with cylindrical shape to ensure the distribution of the largest possible amount of air (Fig. 1). Bioreactors were operated for 3 months to acclimate microorganisms to the laboratory conditions, and to obtain sufficient biomass amount (MLSS) that needed for the study by feeding synthetic culture solution (Table 2). Five aeration pumps were used for getting the dissolved oxygen (DO) concentration of 4-5 mg/L. When MLSS concentration reached to 5000 mg/L, we started to add Ibuprofen by starting the lowest concentration of 0.01 mg/L.

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Table 2: Composition of the synthetic wastewater added to the bioreactors

Chemicals	mg/L	Company produced
$MgSO_4.7H_2O$	60.9	Sigma-Aldrich®
$NaHCO_3$	218.8	Merck
NH_4Cl	38.2	Tekkim
Yeast extract	209.7	Merck
Peptone	184.7	Sigma-Aldrich®
$CH_3COONa.3H_2O$	130.8	Sigma-Aldrich®
KH_2PO_4	35.1	Sigma-Aldrich®
$CaCl_2.2H_2O$	70	Merck
$NaHCO_3$	218.8	Merck

2.2. Batch Reactor System and Daily Experiments

Five aerobic batch reactors (A, B, C, D and control) were used in this study, and their treatment performances were investigated by measuring concentrations of COD, suspended solids (MLSS), SVI, DO and oxygen uptake rate (OUR). The reactors were operated for 52 h period under in the batch mode, and samples were collected at every 12 h time interval. The operational conditions of the bioreactors were shown in Table 3. All reactors have same conditions, but only HRT values were different.

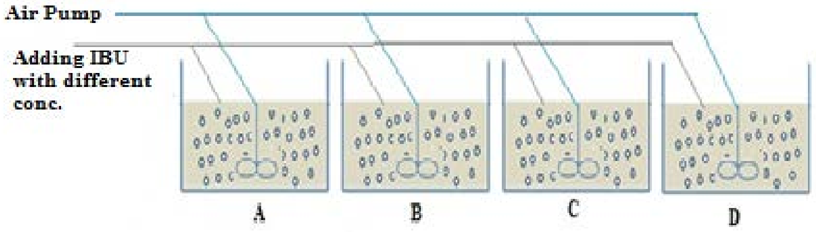


Figure 1: Schematic diagrams of the bioreactors used in study

2.2.1. Sludge Volume Index (SVI)

SVI is an indication of the sludge settle ability in the final clarifier. The common range for an SVI at activated sludge plant should be between 50 and 150 mL/g. SVI values were determined for each experimental according to Equation (1).

$$SVI(\frac{mL}{g}) = settled\ sludge\ volume\ in(\frac{mL}{L}) \times \frac{1000}{MlSS\ (\frac{mg}{L})}. \quad (1)$$

2.2.2. Sludge Age

Sludge age is one of the tools available to the operator to help maintain the desired amount of solids in the aeration tank. The common range for sludge age for a conventional activated sludge plant is between 3 and 15 days. Sludge age is computed by Eq (2):

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$$Sluge\ Age\ (d) = \frac{MLSS(mg/L)}{Primary\ Eff.SS(\frac{mg}{L.d})} \quad (2)$$

2.2.3. The Food/Mass Ratio (F/M)

F/M is based upon the ratio of food fed to the microorganisms each day to the mass of microorganisms held under aeration. The F/M ratio is calculated as Eq. (3):

$$\frac{F}{M} = \left[BOD\ \left(\frac{mg}{L}\right) \times Flow\ \left(\frac{m3}{d}\right)\right] MLSS(\frac{mg}{L})\ldots \quad (3)$$

2.2.4. Oxygen Uptake Rate (OUR) Test

The measurements of the respirometric results of the microorganisms have demonstrated to be a useful tool at wastewater treatment plants in many aspects. The OUR measurements can be performed with using simple equipment, and the data can be used for simpler characterization and process control [14]. We measured OUR values of microorganisms for bioreactors to determine biodegradability of ibuprofen as shown in Fig.2.

2.3. Experimental methods

All the experiments included soluble COD (5220 D. Closed reflux, Colorimetric method), MLSS and MLVSS (2540 G. Total, Fixed and Volatile Solids in Solid and Semisolid samples), TSS (2540 D. Total Suspended Solids dried at 103~105°C), Dissolved Oxygen (DO) (4500-O G. Membrane Electrode method) and pH (4500-H^+ B. Electrometric method) were carried out according to the Standard Methods for Water and Wastewater Examination [15].

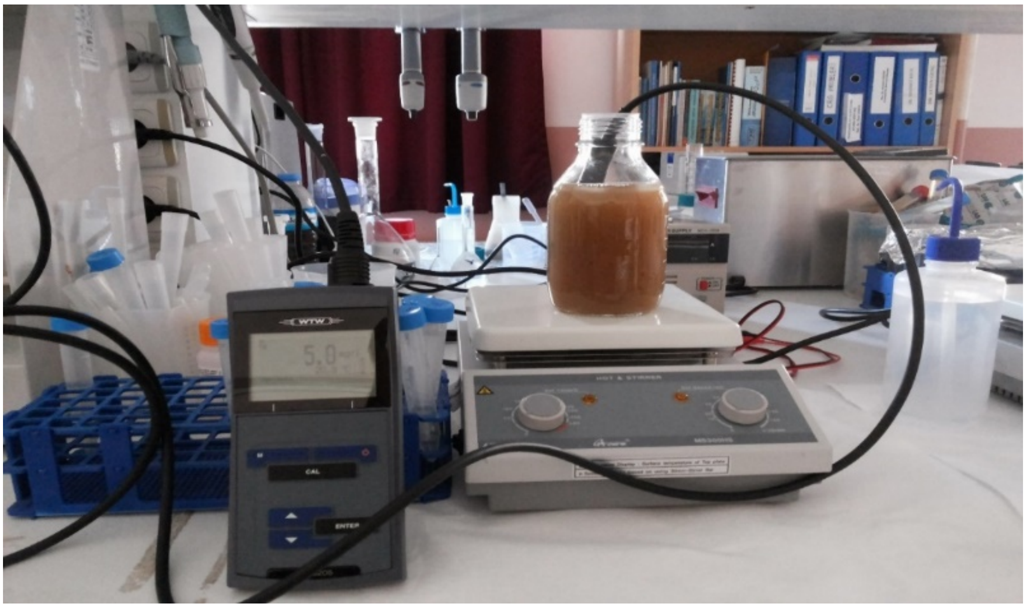


Figure 2. The measurement of OUR in the laboratory

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Table 3: Operational conditions of the bioreactors

Parameters	Time (Months)		
	1-30 days (Avg)	30-60 days (Avg)	Avg.±SD
T°C	22	23	22.6±0.5
pH	6.8	7.1	7.0±0.29
TSS (mg/L)	360	343	351±59.4
COD (mg/L)	667	560	615.2±90
DO (mg/L)	4.0	4.1	4.0±0.26
MLSS (mg/L)	4279	4390	3379±160
MLVSS (mg/L)	2581	2767	2673±200
SVI (mL/g)	93	90	91.5±5.84
F/M (g COD/g MLSS/day	0.20	0.16	0.19±0.029
OUR(mgO_2/L.hour)	26	27	26.3±1.38

2.4. Experimental evaluation for IBU

EPA Method 1694 determines pharmaceuticals and personal care products (PPCPs) in environmental samples by High Performance Liquid Chromatography combined with Tandem Mass Spectrometry (HPLC/MS/MS) using isotope dilution and internal standard quantitation techniques. This method has been developed for use with aqueous, solid, and biosolids matrices (USEPA 2007). 50 mL wastewater samples were taken from bioreactors after each experimental run, stored at refrigerator, and subsequently measured by HPLC.

2.5. Chemicals and Reagents

All reagents used in this study were analytical grade. Ibuprofen obtained from Merck (Germany, 99% purity). Acetonitrile (ACN) and methanol for HPLC grade were purchased from Sigma-Aldrich® (United States), and phosphate buffer from Merck (Germany). Water obtained from Milli-RX apparatus (Millipore, USA) was used to prepare solutions and buffers which were filtered through 0.45 µm Millipore filters prior to use. The sample solutions were filtered through 0.2 µm Minisart® SRP15 Syringe Filters 17559Q (Orange Scientific, Waterloo, Belgium) before the injection into the chromatograph.

2.6. Preparation of the Standards and Calibration Curves

The IBU stock solution was prepared by dissolving 25 mg of pure IBU in 250 mL of ACN to achieve 100 ppm concentration after that calibration standards were prepared by dilution of IBU standard at the following concentrations: 0.1, 0.2, 0.5, 1, 2, 5 and 10 ppm (Fig. 2). All standards were kept at 3± 1°C [16].

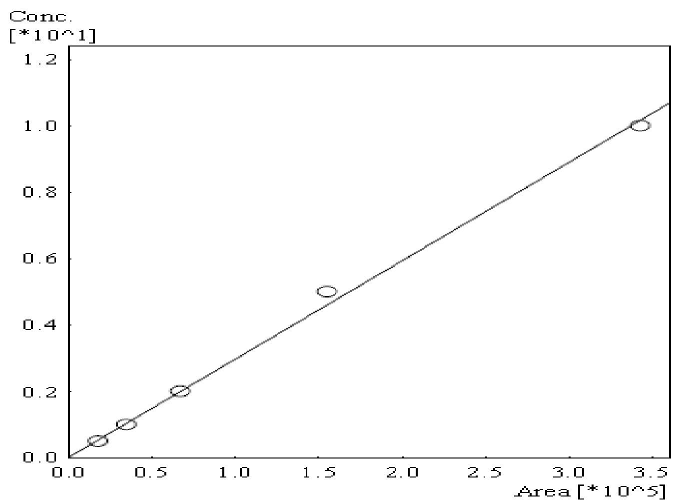


Figure 2: Calibration curve for Ibuprofen used in the HPLC measurements

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2.5. The Solid Phase Extraction (SPE)

Solid phase extraction was performed as described in Jones et al. (2003) using a Waters (Milford, USA) Sep-Pak Vacuum Manifold and a Compton vacuum pump from Dawson, McDonald & Dawson Ltd., (Ashbourne, United Kingdom). After centrifugation of samples which was pulled from bioreactors having different hydraulic retention times, isolated by solid phase extraction using 3 mg Oasis hydrophilic-lipophilic balance cartridges (Waters, United Kingdom). The samples were pre-filtered through glass fiber filters (Scheicher and Schuell). The cartridges were preconditioned with 1 mL ACN and 1 mL of ultra-pure water. The liquid phase was drawn through a cartridge at a flow rate of approximately 5 mL a minute. When the sample had passed through, 4 mL of reagent grade (18.2 mΩ) water (Millipore, Watford, UK) was used to rinse the solid phase, the cartridge was then dried by drawing air through it for 1 h. The cartridges were washed with 1 mL 5% methanol to remove any loosely bound contaminants, and then they were eluted with 2 mL ACN [17].

2.6. HPLC Analysis of Ibuprofen

The wastewater samples were cleaned up using SPE, and then analyzed for ibuprofen by HPLC (Shimadzu LC 20 AT) equipped with a diode array detector (DAD), C18 Colum (250, 4.6 mm, 5 μm). The method summarized in Table 4 was developed as a part of this work. IBU with a purity of 99% was used to produce HPLC standards [18]. The method was successfully applied to the determination of Ibuprofen in the samples. The chromatogram at 210 nm showed a complete resolution of all peaks (Fig. 3).

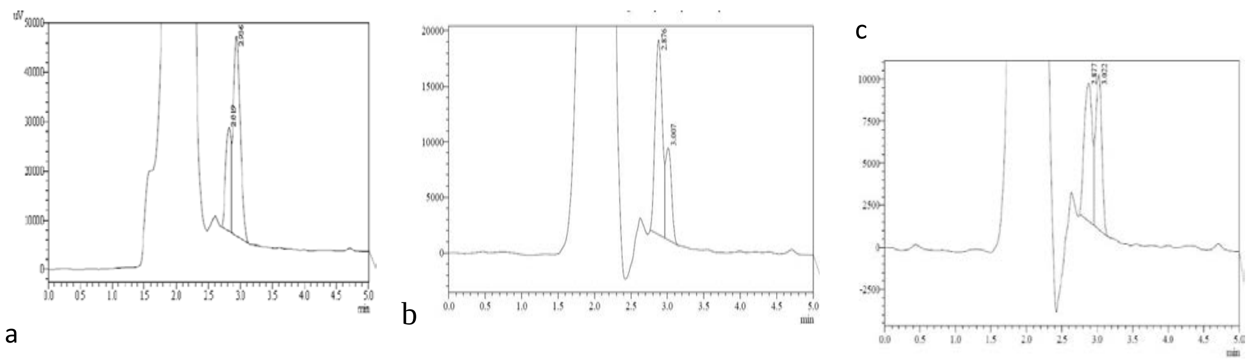


Figure 3. Detection of Ibuprofen by HPLC at different concentrations (a. 10 ppm, b. 5 ppm, c. 2 ppm)

Table 4: The method used to determine IBU residues by HPLC

Chemical	Ibuprofen
Mobil phase	ACN:PB -60:40
Flow rate (mL/ min)	1
Total time (min)	5
T (C°)	40
Retention time (min)	2.8
UV Detection (nm)	210

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3. RESULTS AND DISCUSSION

As stated before, the experimental study was set into five bioreactors operated under the same environmental conditions but at different HRTs. The objective of this research was to determine the ability of extended aerated activated sludge processes to remove more widely used pharmaceuticals products such as Ibuprofen. The effluent qualities and the activated sludge properties of the reactors are summarized in Table 5.

Table 5. The Effluent quality and the sludge properties of EASP

Reactor	**IBU**
Effective Volume (L)	5
pH	7.06±0.29
T (^{0}C)	22.6±0.5
DO (mg/L)	4.03±0.3
SRT (d)	20
HRT (h)	12-52
Effluent COD (mg/L)	615±90
COD removal (%)	89
TSS (mg/L)	351±59
MLSS (mg/L)	3379±160
MLVSS (mg/L)	2673±200
MLVSS/ MLSS (%)	79.1
Excess sludge (g/d)	0.49
F/M Ratio	0.18±0.03
SVI (mL/ g)	66.5±10

3.1. The Sludge Volume Index Results of Bioreactors

Sludge volume index of 100 mL/g is mostly known as the boundary value of sludge having well settling characteristic. All the reactors showed acceptable SVI for the extended activated sludge process. The highest SVI belonged to the control reactor of 100 mL/g while, the lowest one of 51 mL/g belonged to the IBU reactor operated in HRT value of 52 h and 5 mg/L.

3.2. MLSS Results of Bioreactors

Microorganism concentration (MLSS and MLVSS) is important to know the effective performance of a biological processes. We investigated the effect of MLSS concentration in the reactors operated in high HRT value of 52 h, and IBU concentration of 1 mg/L (Fig. 4). As shown in Fig. 4, the high MLSS concentration affected the treatment performance of IBU especially in 5000 mg/L.

3.3. Oxygen uptake rate (OUR) and COD Removal

The OUR results indicated reverse relationship between oxygen uptake rate and chemical complexity/toxicity to the microorganisms. Because these microorganisms need more oxygen to convert the chemicals to simpler compounds. OUR results were in the range of 24-29 mgO_2/L.h for control reactor at different HRT values of 12-52 h. These values were measured in the range of 29-41 mgO_2/L.h for IBU reactor of 1 mg/L. The effluent COD of the reactors decreased with increasing

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HRT values. COD removal efficiency of the reactor operated at HRT of 12 h was found to be 47% while, this value increased to 85% when HRT was increased to 52 h.

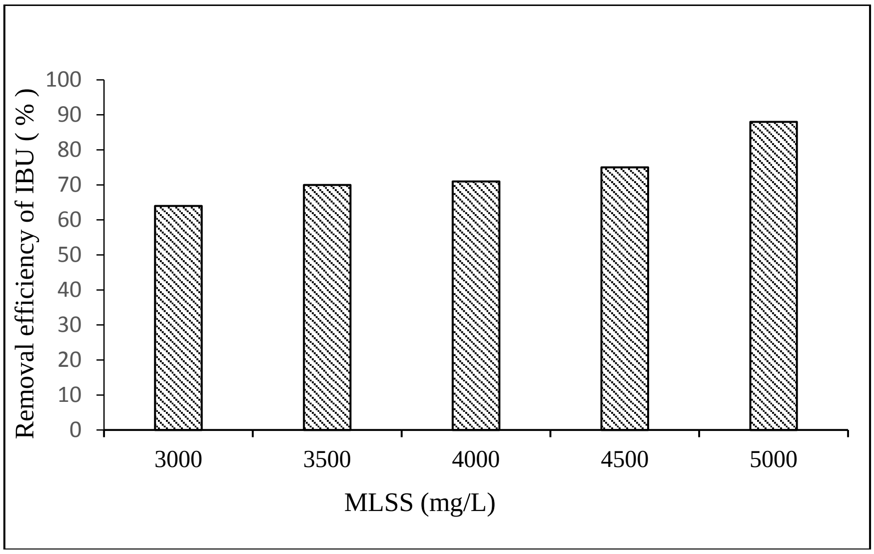


Figure 4. The removal efficiency (%) of IBU (1 mg/L) at different MLSS concentrations

3.4. Ibuprofen Removal

The percentage removal values of IBU for different HRTs were shown in Table 5. According to the results, it can be said that IBU was eliminated entirely during the experimental process with a biodegradation removal efficiency of 99.9% in 52 h. Ibuprofen has shown to be easily removed by the extended aeration active sludge reactor throughout the experiments. Ibuprofen has a low K_d value for secondary sludge (0.007± 0.002) and the highest biological transformation rate (k_{biol}=21-35) of the substances. This means that ibuprofen can be degraded by microorganisms and degradation products of ibuprofen can be created.

Table 5. Ibuprofen removal efficiencies (%) of the reactors at different HRT values

IBU (mg/L)	HRT of reactors (h)				
	0	12	24	36	52
	Ibuprofen Removal %				
0.01	0	77.9	85.0	94.7	99.9
0.02	0	73.2	81.2	93.7	99.9
0.1	0	70.0	79.8	89.0	99.9
0.2	0	67.1	78.0	86.6	99.9
0.5	0	64.1	74.0	82.7	98.1
1	0	59.0	66.0	75.9	89.0
5	0	48.8	62.7	73.1	84.1
10	0	48.0	57.1	69.7	81.8

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4. CONCLUSIONS

The results of the present study exhibited that extended aeration activated sludge reactor can be used for enhanced the removal of Ibuprofen. This may suggest that conventional wastewater treatment technologies are very efficient in completely removing of such bioactive compounds entering to aquatic environment and drinking water supplies. Although, the levels of detected pharmaceuticals in the treated water are quite low, the health risks associated with long term exposure to a large number of pharmaceuticals have to be kept in mind.

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5. REFERENCES

[1] Drinan, J.E., Whiting, N.E., 2001. *Water and wastewater treatment, a guide for the nonengineering professional*, CRC press ISBN: 1-58716-049-0.USA. 311s.
[2] Shaar, H., Clara, M., Gans, O., and Kreuzinger, N., 2010. Micro pollutants removal during biological wastewater treatment and a subsequent ozonation step. *Environmental Pollution*, **158**, 1399-1404.
[3] US-EPA, 2000. *Activated Sludge Process Control Testing*, ESD, Water Compliance Unit, Athens, GA.
[4] Mitić, S.S., Miletić, G.Z., Pavlović, A.N., Arsić, B.B., Živanović, V.V., 2008. Quantitative analysis of ibuprofen in pharmaceuticals and human control serum using kinetic spectrophotometer, *J. Serb. Chem. Soc.* **73(8–9)**, 879–890.
[5] (http://www.medicalnewstoday.com/articles/161071.php) (accessed May 1st, 2016).
[6] Smook, T., Zho, H., Zytner, R.G., 2008. Removal of ibuprofen from wastewater comparing biodegradation in conventional, membrane bioreactor and biological nutrient systems. *Water Science & Technology*, **57**, 1-8.
[7] Urase, T., Kikuta, T., 2005. Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process. *Water Research*, **39 (7)**, 1289–1300.
[8] Lischman, L., Smyth, S.A., Sarafin, K., Kleygwegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Beland, M., Seto, P., 2006. Occurrences and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada. *Science of the Total Environment*, **367**, 544-558.
[9] Thomas, P. M., and Foster, G. D., 2005. Tracking acidic pharmaceuticals, caffeine, and triclosan through the wastewater treatment process. *Environmental Toxicology and Chemistry*, **23**, 25-30.
[10] Ternes, T., Joss, A., Kreuzinger, N., Miksch, K., Lema, J.M., von Gunten, U., McArdell, C.A., Siegrist, H. (2005), Removal of pharmaceuticals and personal care products - Results of the Poseidon Project, Industrial Issues & Technical Treatment Session 2, *78th Annual Technical Exhibition and Conference*, Water Environment Federation WEFTEC, 29th Oct.- 2nd Nov. 2005, Washington DC.
[11] Ternes T.A., Joss A. Siegrist S., 2004. Pharmaceuticals and personal care products: wastewater practice under close scrutiny. *Environ. Sci. Technol*. **15**, 393A-399A.
[12] Suárez, S., Carballa, M., Omil, F. and Lema, J. M., 2008. How pharmaceuticals and personal care products (PPCPs) are removed from urban wastewaters. *Reviews in Environmental Science and Biotechnology*, **7**, 125-138.
[13] Roh, H., Subramanya, N., Zhao, F., Yu, C-P., Sandt, J. and Chu, K.H., 2009. Biodegradation potential of wastewater micro pollutants by ammonia-oxidizing bacteria. *Chemosphere*, **77**, 1084-1089.
[14] Takeshi, K.I., Yuichi, M., Keiichi, E., Katsushi, Y., 2006. Influences of drugs on the oxygen uptake rate and bisorption of activated sludge. *Biol. Pharm. Bull,* **29 (1)**, 183-186.
[15] A.D. Eaton, L.S. Clesceri, A.E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC, 1995.
[16] 40 CFR Part 136, Appendix B to Part 136 - *Definition and Procedure for the Determination of the Method Detection Limit*-Revision 1.11
[17] Ahlgren, P., 2012. *Biodegradation of potentially harmful compounds in wastewater treatment.* Master Thesis, Aalto University Schools of Technology ,115s.
[18] Tixier, C., Singer, H.P., Canonica, S., Mqller, S.R., 2002. Phototransformation of Triclosan in Surface Waters: A Relevant Elimination Process for This Widely Used Biocide Laboratory Studies, Field Measurements, and Modeling. *Environ. Sci. Technol*., **36 (16)**, 3482–3489.

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Sustainable degradation of municipal sludge by using phytochemical molecules with antioxidative activity

E. Giannakopoulos[1], S. Alexandropoulou[1], E. Isari[1], K. Bourikas[1], H. K. Karapanagioti[2], I. Kalavrouziotis[1*]

[1]School of Science and Technology, Hellenic Open University, Tsamadou 13-15 & Saint Andrea, 262 22 Patras, Greece.
[2]Department of Chemistry, University of Patras, Patras 26504, Greece.
*Corresponding author: Email: ikalabro@eap.gr

Abstract

The sustainable degradation of municipal sludge (Biosolids) by co-complexation with phytochemical molecules with antioxidative activity such as polyphenols (PhOH) in alkaline pH under ambient O_2 and temperature is investigated. Physicochemical and structural characteristics of complex (PhOH-Biosolids) are evaluated by UV/Vis diffuse reflectance spectroscopy (DRS) and thermogravimetric analysis (TGA). The comparative analysis among UV/Vis DRS spectra of PhOH and PhOH-Biosolids complex reveals significant differences. This method suggests a novel role of natural RhOH on the degradation, dewatering, and humification of wastes.

Keywords: municipal sludge; degradation; phytochemical molecules; antioxidative activity

1. INTRODUCTION

Today, sewage sludge landfill disposal is not ideal and there is now increasing incentive to economically develop viable reuse and recycling options [1]. A significant amount of research has investigated processing sewage sludge to form new materials such as compost [2].

The management of wastewater sludge, now often referred to as biosolids, accounts for a major portion of the cost of the wastewater treatment process and represents significant technical challenges [3]. In many wastewater treatment facilities, the bottleneck of the sludge handling system is the dewatering operation [4]. Advanced sludge treatment processes such as thermal and thermochemical processes [5], or chemical oxidation using hydrogen peroxide [6] have been developed in order to improve sludge dewatering and to facilitate handling and ultimate disposal. These methods degrade extracellular polymeric substance proteins and polysaccharides reducing their water retention properties [7]. The use of sludge, as raw material for processing into new products such as compost requires the knowledge of the fundamental behaviour of properties and of components (organic and inorganic) of sewage sludge. Approximately 20% of the dry solids of sewage sludge is inert inorganic material and this forms the significant quantity of ash produced by sewage sludge incineration [8].

The phytochemical molecules with antioxidative activity such as polyphenolics (PhOH) represent compounds that have great importance in a wide range of physicochemical and biological processes in humification [9-10]. The UV/Vis spectrum, of these couples in aqueous solutions, is strongly dependent on pH, redox potential E^o, Pb effect, numbers and position of substituents on the phenolic ring. Substituents such as carboxyl (-COOH) and hydroxyl (-OH) groups on the phenol ring can significantly influence the electron density "*on the ring*" and thus modify UV/Vis spectrum dramatically. The UV/Vis spectrum of the PhOH governs the reaction of PhOH with O_2 to form

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free radical $PhO^{-\bullet}$[9-10]. At alkaline pH, the pK_a 's of the PhOH are outstanding indicators of the electron density in the aromatic ring of the members of these triads (electrophilicity) and thus, are excellent tools to predict half-cell reduction potentials for both the one-electron and two-electron couples, which in turn allow estimates of rate constants for the reactions of these triads.

The sustainable degradation of municipal sludge [7] (SL) by co-complexation with phytochemical molecules with antioxidative activity such as PhOH in alkaline pH under ambient O_2 and temperature is investigated. A molecular model which represents the above is the gallic acid (GA, 3,4,5-trihydroxylbenzoic acid). GA is a natural polyphenol which exhibits the most considerable antioxidant capacity in plants and a successful model for the radical properties of natural humic acid at pH>9 [9-10]. The sludge and GA are mixed, under ambient O_2 and temperature at alkaline pH. The complex mechanism is controlled by *UV-Vis* spectroscopy and thermogravimetric analysis (TG). This method suggests a novel role for natural PhOH on the degradation, dewatering and humification of aqueous wastes with a friendly interaction with the environment, as opposed to incineration of sludge.

2. MATERIALS AND METHODS

2.1. Experimental setup

Sewage sludge (Biosolids) at solid phase was collected from Kyparisia municipal wastewater treatment plant in plastic bags and brought to the laboratory.

2.2 Reagents and solutions

All experiments were performed with analytical grade chemicals. Stock, working, and standard solutions and their dilutions were prepared with ultrapure, Milli-Q water, produced by a Millipore Academic system (Millipore, Belford, MA). GA was obtained from Merck (purity > 98.5%, Nr. 842649) and used without further purification.

2.3 UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS). UV-Vis DRS measurements were carried with a Perkin Elmer instrument [11].

2.4. Thermo gravimetric analysis (TGA)

TGA provides an effective alternative to chemical analysis for the chemical characterization of sludges [12-13]. TGA of the dry sludge produced in Kyparisia treatment plant in Greece was carried out under nitrogen atmosphere (flow rate: 200 mL/min) in a Perkin Elmer Diamond Thermogravimetric/ Differential Thermal Analysis (TG/DTA) apparatus. A quantity of the sample (about 10 mg) was placed in a platinum pan at room temperature. Initially the temperature was raised at 100°C and kept constant at this value until moisture removal and weight stabilization. After recording this weight as the initial one, the temperature was increased from 100 to 550°C at a heating rate of 10°C/min. The thermogravimetric (TG) curves were obtained by software.

3. RESULTS AND DISCUSSION

3.1 UV-Vis DRS analysis.

The UV/Vis DRS spectra for Biosolids and (GA–Biosolids) complex are given in Figure 1, after one month *incubation* at pH>9. According to Fig. 1 the UV/Vis DRS spectra of Biosolids and GA-Biosolids show a wide range of bands in the range of 300–800 nm. After mixing among GA and Biosolids, the relative intensity of the bands increases due to the complexation among active groups of Biosolids and of GA species.

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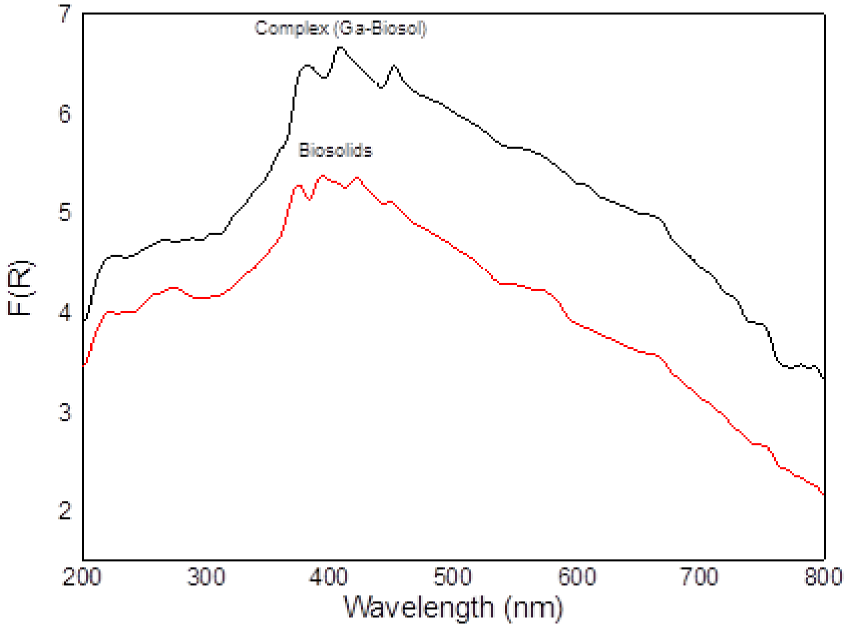


Figure 1. UV–Vis diffuse reflectance spectra for (A) Biosolids and (B) GA–Biosolids

3.2 TG and DTG analysis

Fig. 2 shows the TGA profiles of Biosolids compounds and GA-Biosolids complex. The profiles were normalized according to the initial weight. A comparison among DTG curves showed that the "peak" of GA-Biosolids complex is shifted at higher temperatures compared to "peak" of Biosolids compounds. This shift shows evidence that active groups of the Biosolids compounds and GA-aromatic ring form a strong complex.

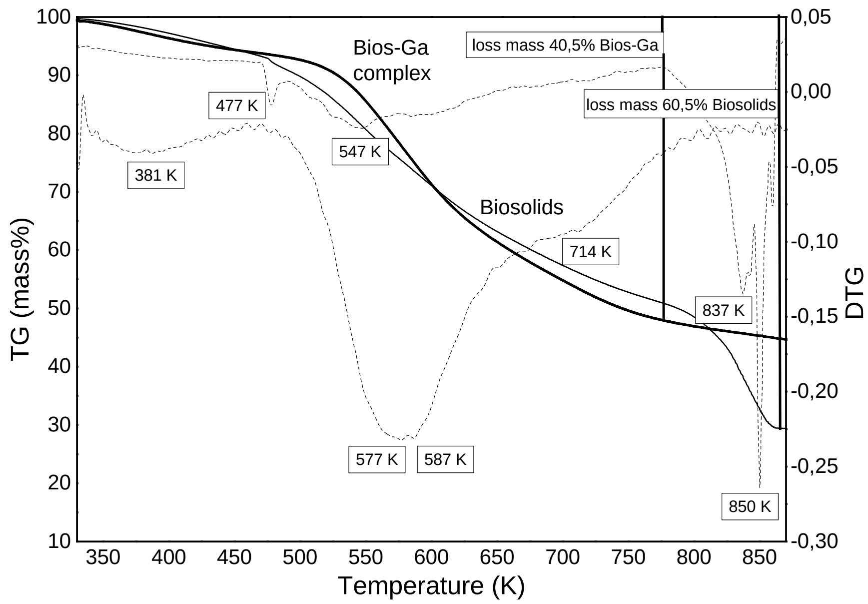


Figure 2: TG (solid curves) and DTG (dotted curves) analysis of Biosolids and GA-Biosolids complex samples conducted in a nitrogen atmosphere.

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CONCLUSIONS

The interaction of phytochemical molecules with antioxidative activity such as PhOH with the Biosolids is a complex process involving adsorption reactions. A comparative analysis for Biosolids and GA-Biosolids complex reveals that the UV/Vis DRS spectra correspond to distinct reactions. These can be assigned to complexation of GA with part molecules of the water soluble extracellular polymeric substances of biosolids by free radicals mechanism. This method is proposed as an environmentally friendly alternative treatment for sludge as opposed to incineration.

References

[1] Ntzala G., Prodromos Koukoulakis H., Papadopoulos H.A., Leotsinidis M., Sazakli E., Kalavrouziotis K.I., 2013. Interrelationships of pollution load index, transfer factor and concentration factor under the effect of sludge, *Int. Journal Environmental Monitoring and Assessment,* **185**(6), 5231-5242.

[2] Kalavrouziotis I.K., Koukoulakis P.H., Ntzala G., Papadopoulos A., 2012. Proposed indices for assessing soil pollution under the application of sludge. *Water Air and Soil Pollution,* **223** (8), 5189-5196.

[3] Kalavrouziotis K.I, Karapanagioti K.H., Leotsinidis M., G. De Feo De G., Sibetheros Y., and Angelakis A., 2014 Ancient Civilizations (WWAC).

[4] Neyens E, Baeyens J, Dewil R, De heyder B., Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, *J Hazard Mater. 2004 Jan 30;**106** (2-3):83-92.*

[5] Neyens E, Baeyens J., A review of thermal sludge pre-treatment processes to improve dewaterability. *J Hazard Mater. 2003 Mar 17;**98**(1-3):51-67 2003*

[6] E. Neyens , J. Baeyens, M. Weemaes,E., Pilot-scale peroxidation (H2O2) of sewage sludge *Journal of Hazardous Materials Volume **98**, Issues 1–3, 17 March 2003, Pages 91–106.*

[7] Neyens E., Dewil R., Heyder De Bart. Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. *Journal of Hazardous Materials **106**B (2004) 83–92, 2004.*

[8] Cheeseman R.C., Sollars J.C., McEntee S., 2003. Properties, microstructure and leaching of sintered sewage sludge ash Resources, *Conservation and Recycling,* **40**, 13–25

[9] Giannakopoulos E., Christoforidis C.K, Tsipis A., Jerzykiewicz M. and Deligiannakis Y. Influence of Pb(II) on the Radical Properties of Humic Substances and Model Compounds. *Journal of Physical Chemistry A 2005, **109**, 2223-2232.*

[10] Giannakopoulos E., Drosos M., and Deligiannakis Y. A Humic Acid-Like Polycondensate Produced With no Use of Catalyst. *Journal of Colloid and Interface Science 2009, **336**, 59-66.*

[11] Hapke, B. 1993. Introduction to the theory of reflectance and emittance spectroscopy. *Cambridge Univ. Press, New York.*

[12] Gómez-Rico M.F., Font R., Fullana A. and Martín-Gullón I., 2005, Thermogravimetric study of different sewage sludges and their relationship with the nitrogen content. *J. Anal. Appl. Pyrolysis,* **74**, 421-428

[13] Jing Wang, Qiang Xue,, 2010. Study on Microscopic Characteristics and Analysis Methods of Municipal Sludge, *EJGE*, **15**, 441-448.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
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The use of colloidal zero valent iron nanoparticles for hexavalent chromium reduction in wastewater: the influence of nitrate

G. Vilardi*, L. Di Palma, N. Verdone

Department of Chemical Engineering Materials Environment,
University of Rome Sapienza, 00184, Rome, Italy.
*Corresponding author: Email: giorgio.vilardi@uniroma1.it

Abstract

The use of nano zero valent iron (nZVI) for groundwater and wastewater remediation is increasingly investigated by several authors thanks to its high potential to reduce heavy metals such as hexavalent chromium. ZVI nanoparticles prepared by conventional methods suffered several problems due to their high reactivity towards surrounding medium; to prevent aggregation and reactivity loss sodium carboxymethyl cellulose (CMC) was used as stabilizer. In this work the reduction capacity of nZVI-CMC colloidal nanoparticles was evaluated at 4 different Fe0/Cr(VI) molar ratio (1.5, 2, 3, 5) through the treatment of different synthetic wastewater solutions (98 mg/L Cr(VI), 58 mg/L Cr(VI), 58 mg/L Cr(VI) and 8 mg/L NO3-, 58 mg/L Cr(VI) and 32 mg/L NO3-, 58 mg/L Cr(VI) and 58 mg/L NO3-) investigating also the influence of other oxidizing species such as nitrate anions. It was possible to estimate the fast reduction thanks to a new method of reaction quenching, utilizing a strong base (NaOH 2M) after each sample withdrawal. The NO3- presence influenced the process producing a slight increase in the chromium reduction at low concentration (from 97.9 to 98.4 % at 1.5 Fe0/Cr(VI) molar ratio) and a significant decrease with the increasing of the concentration (in the presence of 32 mg/L of nitrate the reduction of Cr(VI) decreased from 97.9 to 92.4 % while in the presence of 58 mg/L of nitrate it decreased to 72.6 %).

Keywords: nZVI; hexavalent chromium; CMC; nitrate; reaction quenching.

1. INTRODUCTION

Zero-valent iron (ZVI) particles have been widely applied to environmental remediation, both in soil and groundwater, thanks to its low-cost and ease of use; but due to its chemical and physical properties (large particle size, low specific surface area and short lifetime) the applications characterized by a remarkable efficiency have been limited mostly in shallow groundwater plumes [1]. In the last two decades the researchers focused their attention on the application of nano-sized zero valent iron particles (nZVI), which represents a more adaptable technology for polluted site remediation [2]. The use of nanoparticles grants an increase in the efficiency of the decontamination process mainly thanks to the larger specific surface area, high superficial activity and to the capacity to remain in suspension for long time with the possibility to be injected as colloidal suspension into contaminated zones [3,4]. Typically, nZVI are prepared by reducing Fe(II) or Fe(III) in an aqueous solution using a strong reducing agent ($LiBH_4$, $NaBH_4$) appears most suitable because of its minimal use of environmentally harmful solvents and chemicals. However, due to their high surface area and high reactivity ZVI nanoparticles prepared using traditional methods tend to either agglomerate rapidly or react quickly with the surrounding media resulting in rapid loss in reactivity

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(passivation of the surface) and mobility [5]. Among the three common methods to reduce these risks (second catalytic metal doping [6], chemical stabilization [7] and supporting [8]) the use of carboxymethyl cellulose (CMC) as stabilizer represents the most used one. The molecules of CMC release Na^+ in aqueous solution, adsorb on to the surface of ZVI nanoparticles creating a negative charged layer which prevents the agglomeration thanks to repulsive forces [9]. Indeed this organic stabilizer reduces the toxicity of nZVI towards living organisms as bacteria and fungi [10,11], thanks to the low release of highly toxic reactive oxygen species (ROS) caused by iron corrosion [12,13].

Based on the work of Glavee et al. [14] ZVI nanoparticles were first used by Whang and Zhang [15] at Leigh University USA. Since then ZVI nanoparticles has been proven as significant effective for the removal/degradation of a wide range of chemical pollutants, including: chlorinated pesticides [16]; organophosphates [17]; nitroamines [18]; nitroaromatics [19]; inorganic anions [20] and heavy metals [21,22]. In particular among the various heavy metals, Cr(VI) exhibits high selectivity upon reaction with ZVI [2]. As reported [23], the removal efficiency of zero-valent iron ranked from top to bottom: As > Cr > Cu > Hg > Pb > Zn > Cd > Ni, whereas especially Cr(VI) can react with ZVI by more than one mechanism, i.e., reduction, adsorption, co-precipitation [24]. Hexavalent chromium is a priority pollutant in many countries [25]. Reduction of Cr(VI) to Cr(III) is desirable as the latter species is an essential nutrient for maintaining normal physiological function and also has a low mobility and bioavailability [26]. When Cr(VI), as chromate or dichromate anion, is reduced by nZVI, it precipitates as insoluble hydroxide or co-precipitates with Fe(III) in a mixed oxyhydroxide [27]. Several parameters influence the process, as pH, temperature, the presence of dissolved oxygen, the active surface area and stability of the nanoparticles and the presence and mobility of other ions. Especially the co-presence of nitrate may strongly affect the adsorption/reduction of dichromate ions by nZVI; depending on the NO_3^- concentration, the rate removal of Cr(VI) in water could increase or decrease until the complete inhibition of the reaction. The contemporary presence of chromates and nitrates in groundwaters was observed in several agricultural contaminated land, in proximity of sites associated with metal plating, wood processing, leather tanning, metal corrosion inhibition, and pigment production [28]. The contemporary removal of these two chemical species in water by ZVI nanoparticles was not still investigated and the objective of this work is to study the effective influence of different concentrations of nitrate anions on Cr(VI) removal by colloidal CMC-ZVI nanoparticles, varying also the initial concentration of the contaminant. In addition a kinetic study was also reported.

2. MATERIALS AND METHODS

Sodium nitrate ($NaNO_3$) and potassium dichromate ($K_2Cr_2O_7$) were used as contaminant models in aqueous solution. Iron nanoparticles were synthesized by the reduction of Iron sulphate eptaidrate ($FeSO_4*7H_2O$) with sodium borohydride ($NaBH_4$), and carboxymethylcellulose (CMC) was used as dispersing agent in the ratio CMC/Fe^{2+}=0.005 (mol/mol) according to previous studies [29]. This organic stabilizer reduces also the corrosion of iron nanoparticles by water and residual dissolved oxygen:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (1)$$

$$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O \quad (2)$$

$FeSO_4*7H_2O$ was used as the starting salt instead of the commonly used ferric cloride ($FeCl_3$) because of its two main advanteges: the reduction of ferrous ions needs less borohydride and complexes formed by ferrous ions and CMC are more stable than the complexes formed with ferric

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ones [29]. All the reagents were used without any purification and all the solutions were prepared with deionized water (DI). In brief, the synthesis was carried out in a 500 mL flask where nitrogen (N_2) was purged during the entire preparation. 120 mL of a solution 0.04 M of Fe^{2+}-CMC was prepared and 120 mL of a solution 0.08 M of BH_4^- was added drop wise to the previous one. No buffer systems were used during the preparation or during the experiments. Reaction mixture was shaken vigorously for an hour to let the gas evolution (hydrogen) ceased. The reduction of ferrous ions follows the main equation:

$$2BH_4^- + Fe(H_2O)^{2+} \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \quad (3)$$

according to the neutral-alkaline pH measured (7.78) at the end of the synthesis. To promote the total reduction of ferrous iron, limited by the rapid hydrolysis of sodium borohydride favored at acidic pH [30], the molar ratio BH_4^-/Fe^{2+} was increased to 2.2.

2.1 Experimental procedure

Batch experiments examined the nitrate and Cr(VI) removal from aqueous solutions using ZVI nanoparticles. All tests were carried out on a shaker at 25°C in a 250 mL conical flask. Several solutions were prepared, which differed for NO_3^- and Cr(VI) initial concentrations: initially a nitrate solution (58 mg/L) and two dichromate solutions (58 mg/L and 98 mg/L of Cr(VI)) were tested to investigate the reaction kinetic of contaminants removal alone, using four increasing concentrations of nanoparticles (0.15, 0.2, 0.3, 0.5 g/L which correspond to nZVI/Cr(VI) molar ratio equal to 1.5, 2, 3 and 5 respectively); subsequently three mixed nitrate-dichromate solutions were prepared (8 mg/L NO_3^- + 58 mg/L Cr(VI); 32 mg/L NO_3^- + 58 mg/L Cr(VI), 58 mg/L NO_3^- + 58 mg/L Cr(VI)) and tested using a 0.15 g/L solution of ZVI nanoparticles. Nitrogen was purged inside the reactor during the treatment and the reaction mixture was continuously shaken without any pH control. At various time intervals (0, 1, 2, 3, 4, 5, 10, 15, 30, 45, 60 min) a sample of 2 mL was withdrawn, subsequently 3 mL of the NaOH (2 M) solution were added and the diluted sample was filtered through a 0.45 μm Whatman membrane filter. Anion concentrations were measured by ion chromatography (Dionex ICS – 1100), Cr(VI) concentration was determined using the 1,5 diphenylcarbazide colorimetric method at 540 nm with using a UV-visible spectrophotometry (T80+, PG Instruments, Ltd.). All the experiments were carried out in triplicates to ensure repeatability.

3. RESULTS AND DISCUSSION

3.1 Effect of nZVI concentration and comparison between nitrate and Cr(VI) treatments

Results of Cr(VI) and NO_3^- reduction at the end of the treatment (60 min) are reported in Figures 1 and 2 respectively.

As it is possible to observe, a slight increase in the Cr(VI) reduction occurred increasing the amount of reducing agent used and decreasing the initial concentration of the pollutant. The latter phenomena was due to an overload of the active sites caused by the higher amount of dichromate anions in the solution (similar phenomena has already been observed in TCE degradation by nZVI [31]).

As showed in Figure 2, the increase in nitrate removal percentage with the increase of nZVI amount used is higher than the increase obtained for the Cr(VI) removal. It is not possible to make a comparison, at fixed nZVI amount used, between the anions removal. In fact, according to the following equations [4], the stoichiometric ratio between reducing/oxidizing agent is different for the two chemical species:

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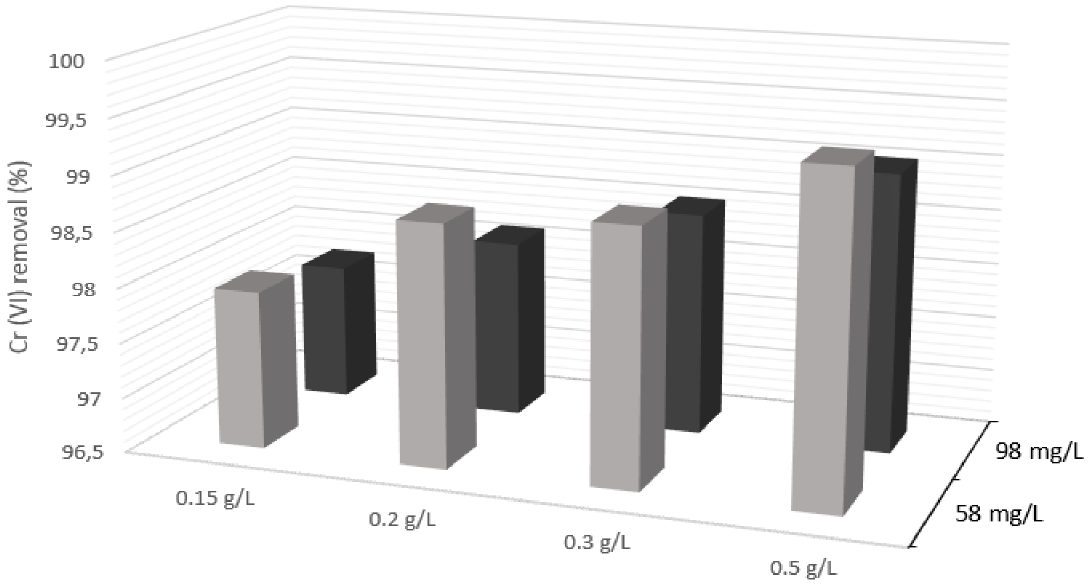


Figure 1. Comparison between Cr(VI) removal values at different nZVI amount (60 min).

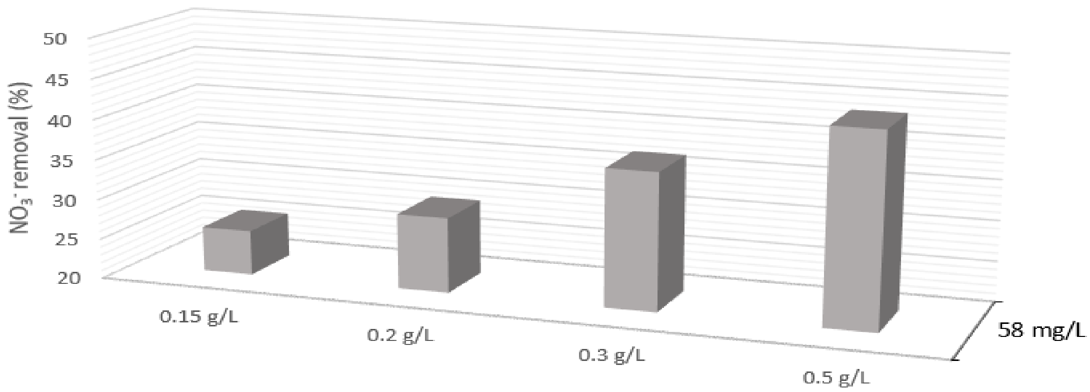


Figure 2. Comparison between NO_3^- removal values at different nZVI amount (60 min).

$$3Fe^0 + Cr_2O_7^{2-} + 7H_2O \rightarrow 3Fe^{2+} + 2Cr(OH)_3 + 8OH^- \qquad (4)$$

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (5)$$

in which it is possible to observe a stoichiometric molar ratio (nZVI/Cr(VI)) equal to 1.5 for the Cr(VI) and a higher value (nZVI/NO_3^-), equal to 4, for the nitrate anion. It means that the stoichiometric amounts of nZVI for Cr(VI) and NO_3^-, according to the initial concentration of 98 mg/L and 58 mg/L of Cr(VI) and NO_3^- respectively, is roughly 0.15 g/L for Cr(VI) and 0.2 g/L for NO_3^-. Therefore, focusing on the efficiency of the two treatments, it is possible to say that nZVI is more suitable for hexavalent chromium reduction than that for nitrate one. The test carried out on nitrate wastewater were prolungated until the asympthotic value was reached (120 min). Figure 3 displays the NO_3^- percentage removal values at 120 min.

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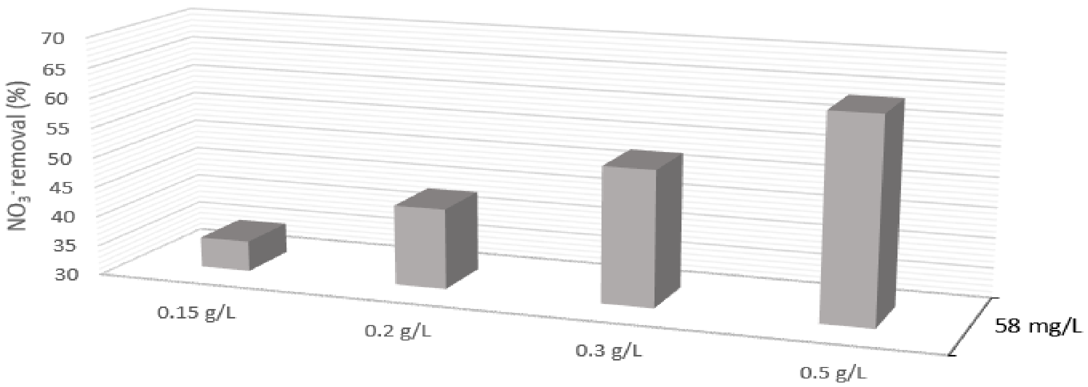


Figure 3. Comparison between NO_3^- removal values at different nZVI amount (120 min).

As showed in the Figure 3, the maximum percentage removal value obtained for a stoichiometric amount is equal to 43.4 %, respect to the 97.9 % obtained for the Cr(VI) removal.

3.2 Influence of nitrate presence on hexavalent chromium reduction

The same treatments were carried out on mixed synthetic wastewater, fixing the nZVI amount used to 0.15 g/L (Figure 4).

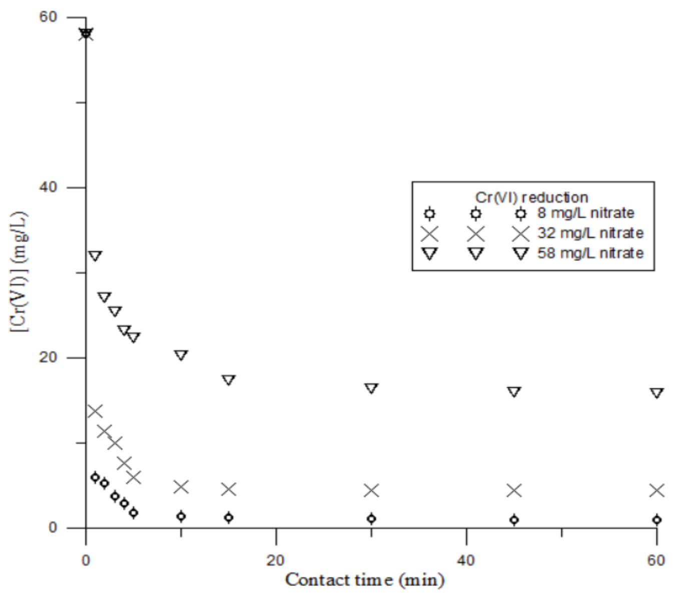


Figure 4. Results of Cr(VI) removal in the presence of increasing amount of nitrate anions.

In Figure 4 it is possible to observe the influence of the presence of nitrate anions on the Cr(VI reduction by nZVI. According to previous studies [1] based on the concentration of co-existing anions in the treated solution, mainly two processes could occur: an increase in the ionic strength of the solution and a competition with dichromate anions for the active sites of the surface of nZVI. In the first treatment, the little amount of nitrate (8 mg/L) is not enough high to let nitrate anions (which are smaller and which are monovalent) compete with dichromate anions; thus the slight

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increase in the Cr(VI) removal (97.9 % to 98.4 %) was explained through the increase in the ionic strength of the solution, according to the following equation:

$$I = 0.5 \sum c_i z_i^2 \quad (6)$$

where I (mol/L) is the ionic strength of the solution, c_i and z_i are the molar concentration and the charge of ion i. Subsequently in the second and third treatment a significant decrease in the Cr(VI) reduction occurred (from 97.9 % to 92.4 % and to 72.6 % in the presence of 32 mg/L and 58 mg/L of nitrate respectively) due to the large amount of competitive anions for the active sites of nZVI. This competitive mechanism was confirmed by the co-reduction of nitrate anions observed in the last two treatments, as showed in Figure 5, where it is possible to observe that the nitrate reduction occurred following the same trend of the Cr(VI) reduction, which is in contrast with the trend observed on the nitrate reduction alone (Figure 6) that follows a pseudo-first-order reduction kinetic, as reported by previous work [4]:

$$Ln[(NO_3^-)] = Ln[(NO_3^-)_0] - k_{obs}t \quad (7)$$

where $(NO_3^-)_0$ (mg/L) is the initial nitrate concentration, t (min) the contact time and k_{obs} (min^{-1}) is the observed rate constant of the pseudo-first-order reduction kinetic.

It could be explained taking into account the rapid passivation of the active surface of the ZVI nanoparticles due to the formation of the Fe(III) hydroxide, mixed Fe(III)-Cr(III) oxy-hydroxide and Cr(III) hydroxide which occurred during the reduction reaction of Cr(VI) [37]. This fast step is due to the as much quick reduction of Cr(VI), which, in the presence of a significant amount of nitrate, occurs at the same time with the nitrate reduction, producing a competitive mechanism between the two chemical species (characterized by a similar redox potential E^0, 1.32 V for nitrate to ammonia [32] and 1.36 V for Cr(VI) to Cr(III) [33]) which grants a partial reduction of the nitrate specie and a higher reduction of Cr(VI) which follows a remarkable passivation of the active surface of the reducing agent; this last phenomena inhibits the well-known continuous nitrate reduction.

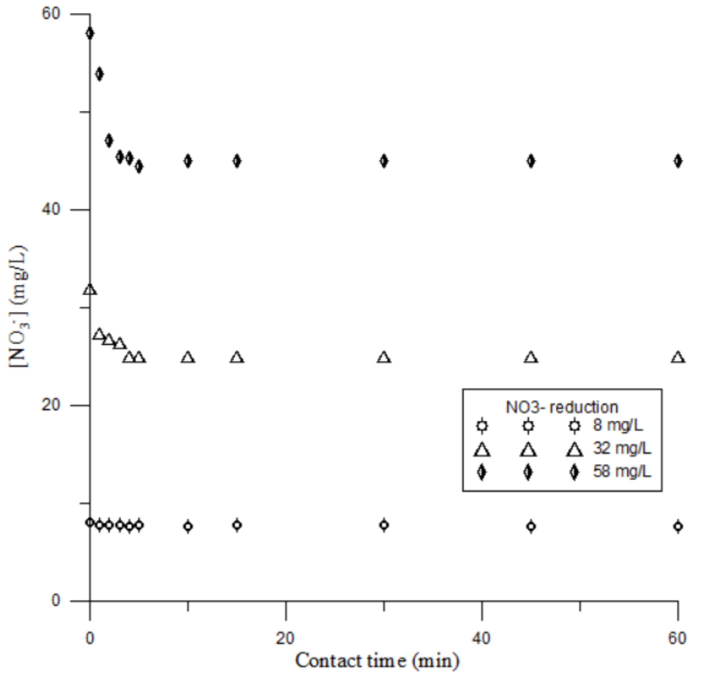


Figure 5. Results of nitrate removal at fixed amount of Cr(VI) and nZVI.

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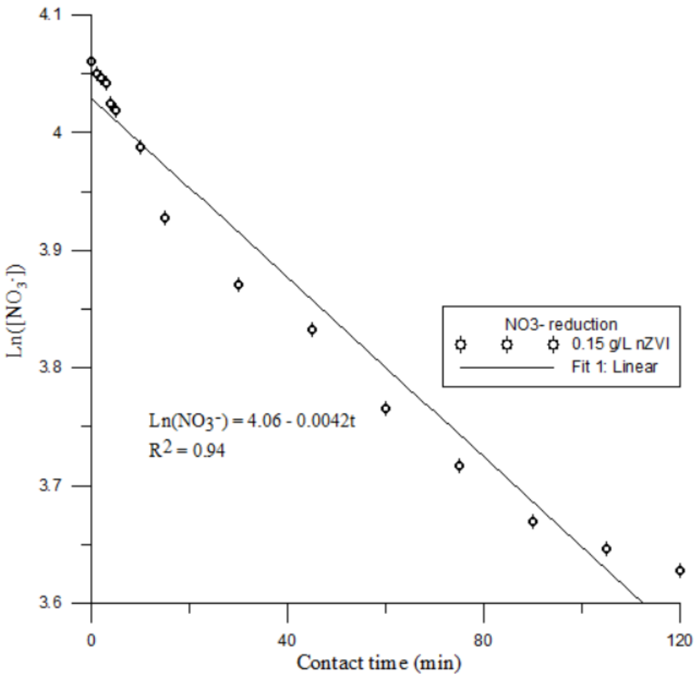


Figure 6. Results of nitrate removal at fixed amount of nZVI.

4. CONCLUSIONS

The reduction of hexavalent chromium performed using colloidal CMC-ZVI nanoparticles proved to be fast, efficient and it strongly depends on the characteristics of the external medium, the characteristics of the nanoparticles and the co-existence of other oxidizing species. As already reported the nitrate reduction follows a pseudo-first-order kinetic whereas the mechanism of chromium reduction seems to be more complex. It proceeds initially very quick, reducing almost the whole amount of Cr(VI) in the first minute to then slows down until the asymptote achievement and the total passivation of the active surface of the nanoparticles. When the co-existence of the two species occurred, the reduction kinetic of Cr(VI) suffered a worsening or an enhancement depending on the concentration and physic-chemical characteristics of the other anion (NO_3^-). In particular it was observed that a small concentration (8 mg/L) of nitrate produced a slight increase in the Cr(VI) reduction (from 97.9 to 98.4 % at 1.5 Fe^0/Cr(VI) molar ratio) thanks to the increase of the ionic strength of the solution, whereas a higher initial nitrate concentration caused the establishment of a competitive mechanism for the active sites of the reducing agent by the two oxidizing species, which produced a decrease in the efficiency of the Cr(VI) reduction (in the presence of 32 mg/L of nitrate the reduction of Cr(VI) decrease from 97.9 to 92.4 % while in the presence of 58 mg/L of nitrate it decreased to 72.6 %). The reported study allow to state in any case the selectivity of nZVI for the dichromate reduction, which shows a remarkable efficiency also in the presence of the same initial concentration of another active oxidizing specie as NO_3^-.

References

[1] Lv, X., Hu, Y., Tang, J., Sheng, T., Jiang, G., Xu, X., 2013. Effects of co-existing ions and natural organic matter on removal of chromium (VI) from aqueous solution by nanoscale zero valent iron (nZVI)-Fe3O4 nanocomposites. *Chemical engineering journal*, *218*, 55-64.

[2] O'Carroll D., Sleep B., Krol M., Boparai H., Kocur C., 2013. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Advances in Water Resources 51, 104-122.

ISBN: 978-960-6865-94-7

[3] Karn, B., Kuiken, T., Otto, M., 2009. Nanotechnology and in situ remediation: a review of the benefits and potential risks. *Environmental health perspectives*, 1823-1831.
[4] Hwang, Y. H., Kim, D. G., Shin, H. S., 2011. Mechanism study of nitrate reduction by nano zero valent iron. *Journal of Hazardous Materials*, *185*(2), 1513-1521.
[5] He, F., Zhao, D., 2005. Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. *Environmental science & technology*, *39*(9), 3314-3320.
[6] Schrick, B., Blough, J. L., Jones, A. D., Mallouk, T. E., 2002. Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoparticles. *Chemistry of Materials*, *14*(12), 5140-5147.
[7] Xu, Y., Zhao, D., 2007. Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water research*, *41*(10), 2101-2108.
[8] Shi, L. N., Zhang, X., Chen, Z. L., 2011. Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. *Water research*, *45*(2), 886-892.
[9] Lv, X., Xu, J., Jiang, G., Xu, X., 2011. Removal of chromium (VI) from wastewater by nanoscale zero-valent iron particles supported on multiwalled carbon nanotubes. *Chemosphere*, *85*(7), 1204-1209.
[10] He, F., Zhao, D., 2007. Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers. *Environmental Science & Technology*, *41*(17), 6216-6221.
[11] Lee, C., Kim, J. Y., Lee, W. I., Nelson, K. L., Yoon, J., Sedlak, D. L., 2008. Bactericidal effect of zero-valent iron nanoparticles on Escherichia coli. *Environmental science & technology*, *42*(13), 4927-4933.
[12] Diao, M., Yao, M., 2009. Use of zero-valent iron nanoparticles in inactivating microbes. *Water research*, *43*(20), 5243-5251.
[13] Keenan, C. R., Sedlak, D. L., 2008. Factors affecting the yield of oxidants from the reaction of nanoparticulate zero-valent iron and oxygen. *Environmental science & technology*, *42*(4), 1262-1267.
[14] Glavee, G. N., Klabunde, K. J., Sorensen, C. M., Hadjipanayis, G. C., 1995. Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and nonaqueous media. Formation of nanoscale Fe, FeB, and Fe2B powders. *Inorganic Chemistry*, *34*(1), 28-35.
[15] Wang, C. B., Zhang, W. X., 1997. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental science & technology*, *31*(7), 2154-2156.
[16] Elliott, D. W., Lien, H. L., Zhang, W. X., 2009. Degradation of lindane by zero-valent iron nanoparticles. *Journal of Environmental Engineering*, *135*(5), 317-324.
[17] Satapanajaru, T., Anurakpongsatorn, P., Pengthamkeerati, P., Boparai, H., 2008. Remediation of atrazine-contaminated soil and water by nano zerovalent iron. *Water, air, and soil pollution*, *192*(1-4), 349-359.
[18] Naja, G., Halasz, A., Thiboutot, S., Ampleman, G., Hawari, J., 2008. Degradation of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) using zerovalent iron nanoparticles. *Environmental science & technology*, *42*(12), 4364-4370.
[19] Choe, S., Lee, S. H., Chang, Y. Y., Hwang, K. Y., Khim, J., 2001. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe 0. *Chemosphere*, *42*(4), 367-372.
[20] Muradova, G. G., Gadjieva, S. R., Di Palma, L., Vilardi, G., 2016. Nitrates Removal by Bimetallic Nanoparticles in Water. *Chemical Engineering Transactions*, *47*, 205-210.
[21] Gueye, M. T., Di Palma, L., Allahverdeyeva, G., Bavasso, I., Petrucci, E., Stoller, M., Vilardi, G., 2016. The Influence of Heavy Metals and Organic Matter on Hexavalent Chromium Reduction by Nano Zero Valent Iron in Soil. *Chemical Engineering Transactions*, *47*, 289-294.
[22] Mystrioti, C., Sparis, D., Papasiopi, N., Xenidis, A., Dermatas, D., Chrysochoou, M., 2015. Assessment of polyphenol coated nano zero valent iron for hexavalent chromium removal from contaminated waters. *Bulletin of environmental contamination and toxicology*, *94*(3), 302-307.
[23] S.-C. Tsai, 2012. Heavy Metal Removal From Water by Zero-valent Iron. Department and Graduate Institute of Environmental Engineering and Management, (Master's Thesis).
[24] Petala, E., Dimos, K., Douvalis, A., Bakas, T., Tucek, J., Zbořil, R., Karakassides, M. A., 2013. Nanoscale zero-valent iron supported on mesoporous silica: Characterization and reactivity for Cr (VI) removal from aqueous solution. *Journal of hazardous materials*, *261*, 295-306.
[25] Di Palma, L., Mancini, D., Petrucci, E., 2012. Experimental assessment of chromium mobilization from polluted soil by washing. *Chemical Engineering Transaction*, *28*, 145-150.
[26] Di Palma, L., Gueye, M. T., Petrucci, E., 2015. Hexavalent chromium reduction in contaminated soil: a comparison between ferrous sulphate and nanoscale zero-valent iron. *Journal of hazardous materials*, *281*, 70-76.
[27] Li, X. Q., Cao, J., Zhang, W. X., 2008. Stoichiometry of Cr (VI) immobilization using nanoscale zerovalent iron (nZVI): a study with high-resolution X-ray photoelectron spectroscopy (HR-XPS). *Industrial & Engineering Chemistry Research*, *47*(7), 2131-2139.
[28] Kavanaugh, M. C., 1994. *Alternatives for Ground Water Cleanup*. National Acad. Press.
[29] He, F., Zhao, D., Liu, J., Roberts, C. B., 2007. Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Industrial & Engineering Chemistry Research*, *46*(1), 29-34.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[30] Davis, R. E., Bromels, E., Kibby, C. L., 1962. Boron hydrides. III. Hydrolysis of sodium borohydride in aqueous solution. *Journal of the American Chemical Society*, *84*(6), 885-892.
[31] Reisner, D. E., Pradeep, T., 2014. Aquananotechnology: Global Prospects, 1st ed., CRC Press.
[32] Westerhoff, P., 2003. Reduction of nitrate, bromate, and chlorate by zero valent iron (Fe 0). *Journal of Environmental Engineering*, *129*(1), 10-16.
[33] Montesinos, V. N., Quici, N., Halac, E. B., Leyva, A. G., Custo, G., Bengio, S., Zampieri, G., Litter, M. I., 2014. Highly efficient removal of Cr (VI) from water with nanoparticulated zerovalent iron: Understanding the Fe (III)–Cr (III) passive outer layer structure. *Chemical Engineering Journal*, *244*, 569-575.

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Uranium removal from aqueous solutions by *Luffa cylindrica* biochar fibres

I. Liatsou*, G. Michael, I. Pashalidis

Department of Chemistry, University of Cyprus, P.O. Box 20537, Cy-1678 Nicosia, Cyprus
*Corresponding author: Email: liatsou.ioanna@ucy.ac.cy

Abstract

The sorption efficiency of biochar fibres regarding the removal of hexavalent uranium [U(VI)] from aqueous solutions has been investigated by batch experiments, as a function of various physicochemical parameters and Fourier transform infrared spectroscopy (FTIR). The biochar fibres have been prepared from the sponge of *Luffa cylindrica* through thermal treatment and they were activated after chemical treatment of the fibres with 8 M HNO_3 for 3 h. The experimental results show that even under strong acidic conditions ($1 < pH < 2$) the relative sorption of the fibres is above 80% while the optimum pH range lies between 5 and 7. The activated biochar fibres obtained from *Luffa cylindrica* show increased sorption capacity for U(VI) (q_{max}= 92 g·kg^{-1}) even at pH 3, which is attributed to the formation of inner-sphere complexes with the surface carboxyl groups of the bio-sorbent. The formation of the inner-sphere complexes is indicated by the effect of ionic strength and it is proven through FTIR spectroscopy.

Keywords: uranium; waters; activated biochar fibres; sorption capacity; FTIR spectra

1. INTRODUCTION

Uranium is a ubiquitous natural element with an average concentration in earth's crust of about 3 mg·kg^{-1} and 3 mg·kg^{-1} in oceans [1]. Additionally, it is the second heaviest naturally occurring radioactive element [2]. Nevertheless, pollution of the environment with uranium and associated health effects have recently become of major concern, particularly due to the use of depleted uranium in military applications [3]. Uranium in environmentally relevant concentrations is found near to uranium mining and processing facilities and usually involves large volumes of wastewater. Cost effective remediation technologies (e.g. ion exchange, reduction, reduction followed by chemical precipitation, electrochemical precipitation, biosorption and adsorption) are required for the removal of uranium from such large volumes of wastewater [2].

Amongst the previous technologies, adsorption with activated carbon and biochars is more attractive for the removal of heavy metal ions, such as U(VI) and the treatment-purification of waters, because of their large surface area and the high affinity of their surface groups for polyvalent metal ions. However, the relatively high production costs make the use of activated carbon impractical for the treatment of large quantities of wastewater. On the other hand, biomass, which is abundant in nature or is produced in large quantities as a by-product or waste from agricultural activities, could be a viable source for biochars production.

Lingocellulosic materials are suitable for conversion into activated carbon because of their high hardness and density, which render them as far better precursors. Moreover, the efficiency of the materials can be enhanced by oxidizing the surface of the carbon in order to increase the number of the surface active sites (e.g. carboxylic and phenolic groups).

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The present study deals with the sorption of hexavalent uranium [U(VI)] by activated biochars prepared from *Luffa cylindrica* fibres. Because of their fibrous structure *Luffa cylindrica* fibres as precursor material, are expected to result in a relatively robust, low-cost product with large external surface available for sorption [4]. The sorption of U(VI) on the activated biochars was curried out by conventional batch experiments and was investigated by FTIR spectroscopy in order to better characterize the surface-bound species and evaluate the thermodynamic parameters (e.g. Kd, ΔG, ΔH and ΔS), which are of fundamental importance for both the assessment of the chemical behavior of uranium in heterogeneous aquatic systems and the development of water treatment technologies related to (radio)toxic metal ion removal.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

All experiments were performed at room temperature (23 ± 2 ^oC) under normal atmospheric conditions in 0.1 M $NaClO_4$ aqueous solutions. The preparation of the test solutions was carried out by dissolution of an appropriate amount of a U(VI) stock solution (0.1 $mol \cdot L^{-1}$) in the desired aqueous solution. The U(VI) stock solution (0.1 $mol \cdot L^{-1}$) was prepared by dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water. The adsorbent used in this study was activated biochar prepared from *Luffa cylindrica* fibres, which were separated from the seeds inside the dried sponges.

2.2 Preparation and characterization of the activated biochar prior and after the [U(VI)] sorption

Luffa cylindrica fibres were collected from a local *Luffa cylindrica* field. The fibres were thermally treated for 1h at 700 ^oC under nitrogen to obtain the carbonized product (biochar). Activation took place by suspending the carbonized product in concentrated nitric acid (8 M HNO_3) for 3 h at 80 ^oC (reflux under continuous stirring). Then the product was washed several times with distilled water and the neutralized material was dried in the oven at 100 ^oC. The dried activated biochar was ground, then the ground product was sieved and the particle fraction between 200 and 500 μm was selected for the adsorption experiments.

The characterization of the *activated biochar prior and after U(VI) sorption* was performed by Fourier transform infrared spectroscopy (FTIR spectrometer 8900, Shimadzu). FTIR measurements were performed by means of translucent KBr disks including finely ground biomass, at a 10:1 mass ratio. In addition, acid/base titrations were performed to study the acid/base behaviour and determine the proton exchange capacity of the activated biochar. That said, suspensions of 0.05 g activated biochar in 20 mL distilled water, were titrated with a pH meter (Hanna Instruments) equipped with a glass electrode by adding small aliquots of 0.1 $mol \cdot L^{-1}$ NaOH until the desired pH was reached. Similar acid/base titrations were also performed with distilled water samples.

2.3 Adsorption studies

Adsorption studies were conducted by means of batch-equilibrium experiments in polyethylene (PE) screw-cap bottles containing a certain amount of biochar (0.01 g) in contact with 30 mL of an aqueous *U(VI)* solution of known total *U(VI) concentration.* The test solutions containing the mixture of the metal ion and the activated biochar were shaken in a thermostated orbital shaker (at 100 rpm) for 24 hours *to assure* that *equilibrium* had been reached. The effect of pH was studied in the pH range between 1.5 and 8, at constant U(VI) concentration ($[U(VI)]_o = 5 \cdot 10^{-4}$ $mol \cdot L^{-1}$) in the suspension and at room temperature (T = 23 ± 2 ^oC). The pH was adjusted by addition of 0.1 $mol \cdot L^{-}$

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[1] NaOH or 0.1 $HClO_4$ $mol·L^{-1}$.For studying the effect of initial U(VI) concentration, the latter was varied between 10^{-5} $mol·L^{-1}$ and $9·10^{-3}$ $mol·L^{-1}$ in the test suspensions, at pH 3 and 5.5. The effect of temperature was studied between 30 and 70 °C using test suspensions (0.01 g biochar in 30 mL solution, $[U(VI)]_o = 5·10^{-4}$ $mol·L^{-1}$) at pH 3 and 5.5. For the kinetic studies certain amount of the activated biochar (0.03 g) was mixed with 100 mL of U(VI) solution ($[U(VI)]_o$ $5·10^{-4}$ $mol·L^{-1}$, T= 23 ± 2 ^oC) at pH 3 and 5.5 and the metal concentration was determined at regular time steps. Finally, the effect of ionic strength was studied in the range between 0.001 and 1 M using test suspensions (0.01 g biochar in 30 mL solution, $[U(VI)]_o = 5·10^{-4}$ $mol·L^{-1}$, T = 23 ± 2 ^oC) at pH 3 and 5.5. As background electrolyte for ionic strength adjustments $NaClO_4$ solutions were used.

The analytical U(VI) concentration in the test solutions was determined spectrophotometrically (UV 2401 PC Shimadzu) by means of arsenazo-III, according to a previously described method [5]. Prior to concentration determination the test solutions were filtrated using 450 nm membrane filters. pH measurements were performed by a commercial glass electrode (Sentek), which was calibrated prior and after each experiment using a series of buffer solutions (pH 2, 4, 7 and 10, Scharlau). For each test solution, a corresponding reference solution was prepared and was similar to the test solution except that it didn’t contain the adsorbent material.

The relative amount of U(VI) adsorbed was determined using the Equations 1 and 2:

$$\text{rel. adsorption\%} = 100 \cdot \frac{([U(VI)]_o - [U(VI)]_{aq})}{[U(VI)]_o} \quad (1)$$

$$K_d = \frac{([U(VI)]_o - [U(VI)]_{aq})}{[U(VI)]_{aq}} \cdot \frac{V}{m} \quad (L \cdot kg^{-1}) \quad (2)$$

(2)

Where: $[U(VI)]_o$ is the total uranium concentration ($mol·L^{-1}$) in the system or in the reference solution, $[U(VI)]_{aq}$ is the uranium concentration ($mol·L^{-1}$) in the test solution, V (L) is the volume of the test solution and m (kg) is the mass of the adsorbent.

Furthermore, the K_d values have been used together with the linear form of the Van’t Hoff equation (Equation 3) and the Gibbs free energy isotherm equation (Equation 4) to estimate the corresponding thermodynamic data [6].

$$\ln K_d = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R} \quad (3)$$

$$\Delta G^0 = -R \cdot T \cdot \ln K_d \quad (4)$$

2.4 Data analysis and uncertainty

All experiments were performed in triplicate and the data are presented as mean ± standard deviation. The uncertainty of the values was generally below 10% and is basically attributed to the error associated with analytical method used (e.g. spectrophotometry using arsenazo-III). The analytical error was determined by the method calibration performed daily using seven reference solutions of various analyte concentrations. Differences between the *means* of two groups *were* analyzed by Student's t test at 95% confidence level. Generally, data analysis and plotting of diagram was performed using Kaleidagraph, a graphing and data analysis software.

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3. RESULTS AND DISCUSSION

3.1 Characterization of the activated biochar prior and after U(VI) sorption

Figure 1 shows the acid/base titration curves corresponding to aqueous suspensions of the activated biochar, as well as the acid/base titration of distilled water. The titration curve corresponding to the activated biochar differs significantly from the titration curve of distilled water indicating the presence of acidic groups on the surface of the activated material. Moreover, the inflection point of the titration curve enables the evaluation of the proton exchange capacity associated with oxygen-containing acidic surface functional groups. The proton exchange capacity has been evaluated to be 5.4 ± 0.3 meq·g^{-1}.

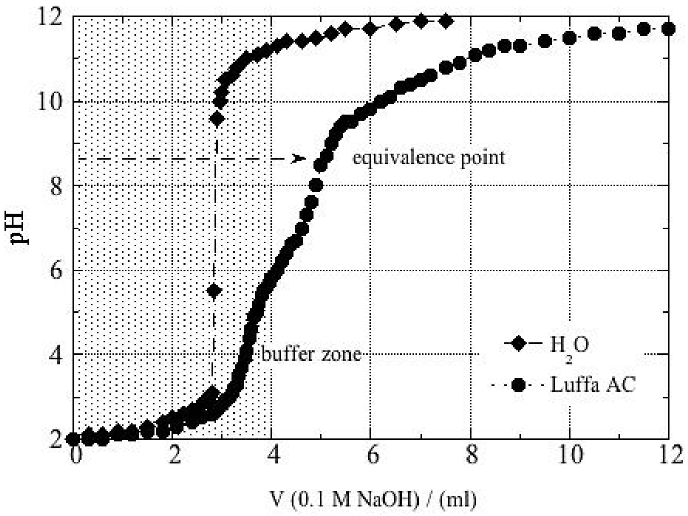


Figure 1. Acid/base titration curves of the activated biochar and distilled water.

Figure 2 shows the FTIR spectrum of the activated biochar prior to U(VI) sorption. The spectrum shows characteristic IR absorption bands at 3405 cm^{-1}, 1717 cm^{-1}, 1599 cm^{-1} and 1220 cm^{-1}, which are attributed to -OH stretching vibrations, carbonyl stretching vibrations, carboxylic acid antisymmetric stretching vibrations and carboxylic acid bending vibrations, respectively [7]. Therefore, the FTIR spectrum of the activated material indicates clearly that HNO_3 activation results predominantly in the formation of carboxylic moieties on the carbonized fibre surface.

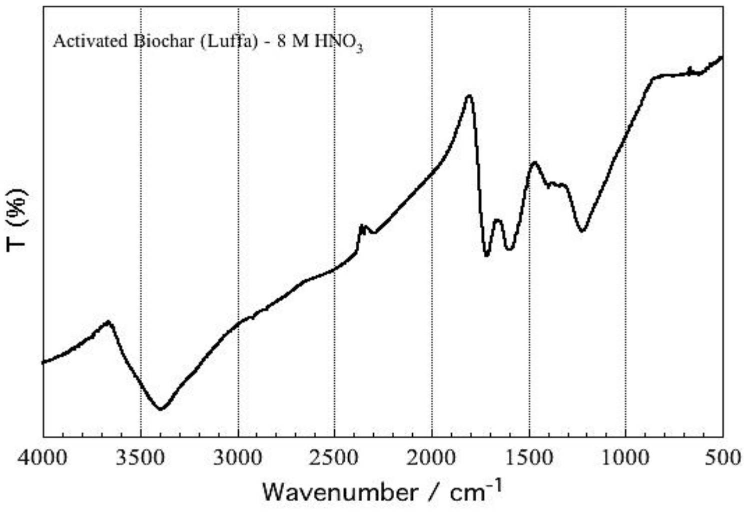
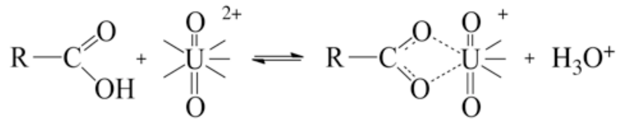


Figure 2. IR spectrum of the activated biochar.

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Figure 3 shows FTIR spectra of the activated biochar with decreasing U(VI) sorbed on the material at pH 3. According to Figure 3 there is a remarkable change in the IR spectra and particularly at wavenumbers corresponding to carbonyl stretching (1726 cm^{-1}), carboxylic acid antisymmetric stretching (1596 cm^{-1}) and carboxylic acid bending vibrations (triple peak between 1145 and 1080 cm^{-1}). Moreover, the intensity of the peak at 930 cm^{-1} increases with increasing concentration of the sorbed U(VI) and indicates clearly that this peak corresponds to the stretching vibration of the O=U=O moiety [8]. In addition, the relative decrease of the band at 1726 cm^{-1} with increasing U(VI) concentration indicates direct interaction between U(VI) and the carboxylic group and the formation of inner-sphere complexes. Assuming only sorption of monomeric species on the biochar surface and taking into account the species distribution of hexavalent uranium under the given conditions, the sorption reaction can be described schematically by Equation 5 [9-11]:



(5)

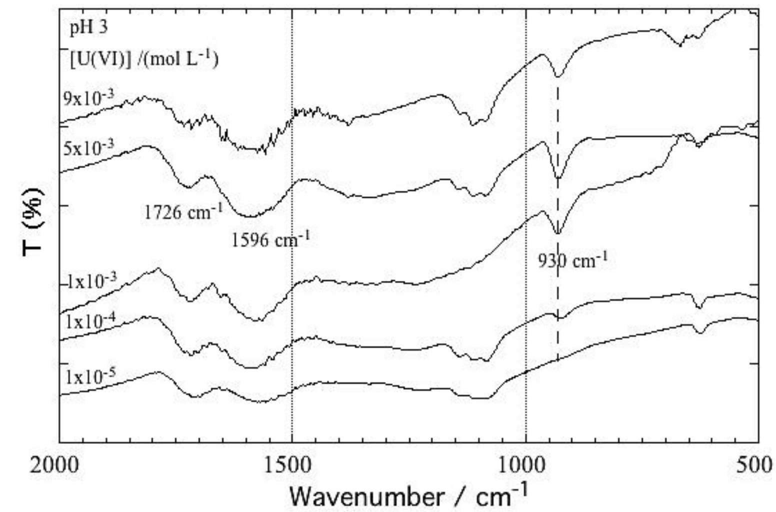
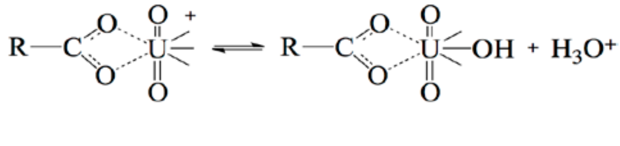


Figure 3. IR spectra of the activated biochar after U (VI) sorption at pH 3 and varying uranium concentration.

The corresponding FTIR spectra at pH 5.5, which are shown in Figure 4, indicate that the sorbed species formed in the near neutral pH suspensions are very similar to the species formed under acidic conditions. Specifically, the characteristic peak of the O=U=O stretching vibration is shifted to lower wavelengths (~ 10 cm^{-1}). This shift could be attributed to the formation of a neutral surface species due to the de-protonation of a U(VI)-coordinated water molecule with increasing pH, as schematically described by Equation 6.



(6)

With increasing pH the neutral surface species which is formed is expected to be more stable than the corresponding charged species. Furthermore, at pH 5.5 and total U(VI) concentration above $1x10^{-4}$ $mol{\cdot}L^{-1}$ the uranium solution becomes oversaturated and besides U(VI) sorption the

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formation of a U(VI) yellow solid phase is observed. Based on the FTIR spectra obtained and the physic-chemical conditions, the solid phase formed is assumed to be $UO_2(OH)_2$ [8].

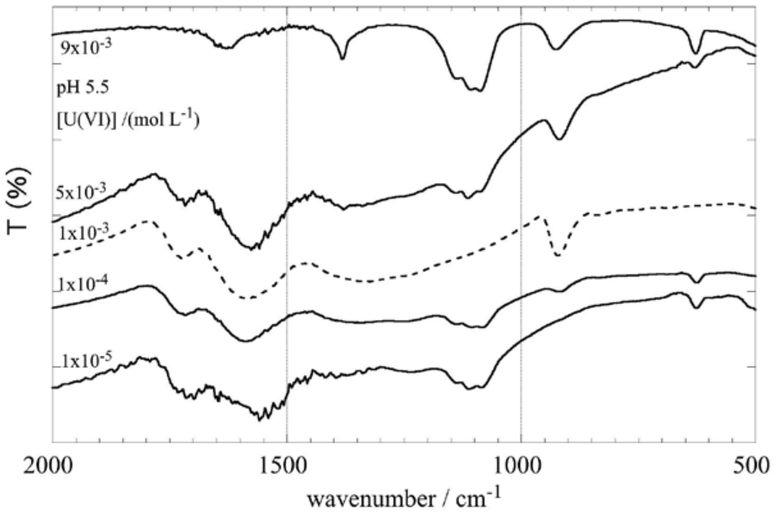


Figure 4. IR spectra of the activated biochar after U (VI) sorption at pH 5.5 and varying uranium concentration.

3.2 Adsorption studies

3.2.1 Effect of pH

According to the FTIR spectra of the activated biochar the binding of UO_2^{2+} on the activated biochar occurs through complexation by the carboxylic moieties found on the activated biochar's surface. Hence, the chemical behaviour of U(VI) in solution and the surface charge of the adsorbent are important parameters affecting the relative adsorption. The solution pH governs both the chemical behaviour of the metal ion in solution and the surface charge of the adsorbent and therefore it strongly affects the sorption on surfaces. To study the effect of pH on the U(VI) sorption, samples of the activated biochar were conducted with U(VI) solutions at different pH values ($1.5 < pH < 8$).

The effect of pH on the relative adsorption of U(VI) by the activated biochar is shown in Figure 5. According to this figure the relative removal increases with increasing pH and reaches a maximum value (~ 95%) in the pH range between 5 and 7.5. At higher pH values U(VI) removal is reduced because of the formation of anionic hydroxo or carbonate uranium complexes in solution [12]. For pH values below 5 the relative adsorption decreases with pH and its value becomes about 80% for pH 1.5. At pH < 6, U(VI) is basically present in the form of positively charged aqueous species [9, 10] and the surface negatively charged, consequently, the sorption of the metal ion is governed by cation exchange reactions. However, with decreasing pH the surface charge is gradually neutralized resulting in lower removal efficiency. Nevertheless, even at pH 1.5 the value of the relative removal is remarkable (~ 80%) suggesting that the activated biochar could be effectively used for the removal of U(VI) even from acid water solutions.

3.2.2 Effect of the initial U(VI) concentration

In order to evaluate the maximum sorption capacity (q_{max}), adsorption experiments with varying U(VI) concentrations have been performed at pH 3 and pH 5.5. The corresponding isotherms are graphically shown in Figures 6a and 6b and indicate that activated biochar derived from *Luffa cylindrica* fibres presents increased adsorption capacity for U(VI). The surface saturation is reached

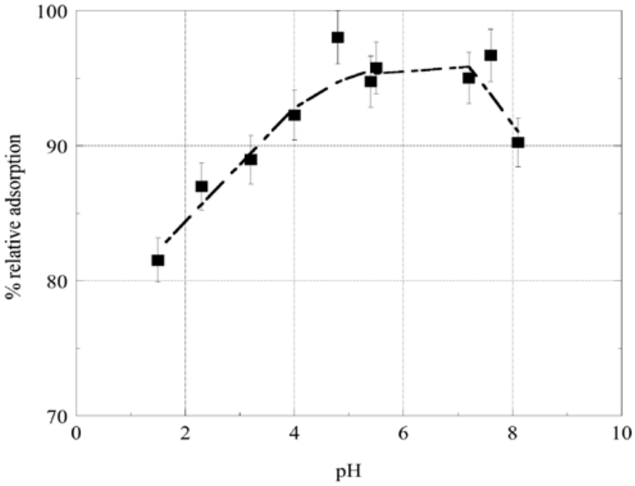


Figure 5. Effect of pH on the U(VI) sorption on activated biochar (0.01 g of biochar, $[U(VI)]_o = 5\cdot10^{-4}$ mol·L^{-1}, I = 0.1 mol·L^{-1} $NaClO_4$, T = 23 ± 2 ^oC, 24 h of reaction time).

for pH 3 at 0.3 mol·kg^{-1} (q_{max}= 92 g·kg^{-1}) and at higher concentrations of the metal the relative sorption increases dramatically suggesting surface polymerization. The uranium concentration in solution is below the concentration defined by the solubility and as a result, no precipitation is expected [9, 10]. The adsorption data prior polymerization are well fitted by the Langmuir isotherm model (R = 0.95), indicating different types of interaction between the surface active groups and the U(VI) cations [13, 14]. Regarding the experimental data at pH 5.5, there is no clear indication for surface saturation because the solubility product is being rapidly exceeded and for $[U(VI)]_o \geq 1$ x 10^{-3} mol·L^{-1} precipitation of $UO_2(OH)_2$ as separate yellow solid phase is observed [8, 10]. Hence, the experimental data cannot be fitted by adsorption isotherms.

The experimental data clearly shows that the activated biochar derived from *Luffa cylindrica* fibres presents, even at pH 3, significantly higher adsorption capacity compared to activated biochars obtained from other biomass by-products (0.4 g·kg^{-1} < q_{max} < 271 g·kg^{-1}) [15, 16]. This high adsorption capacity of the activated biochar is attributed to the fibrous vascular system of *Luffa cylindrica*, which provides to the sorbent extended surface for relatively rapid fluid exchange and increased sorption capacity [17].

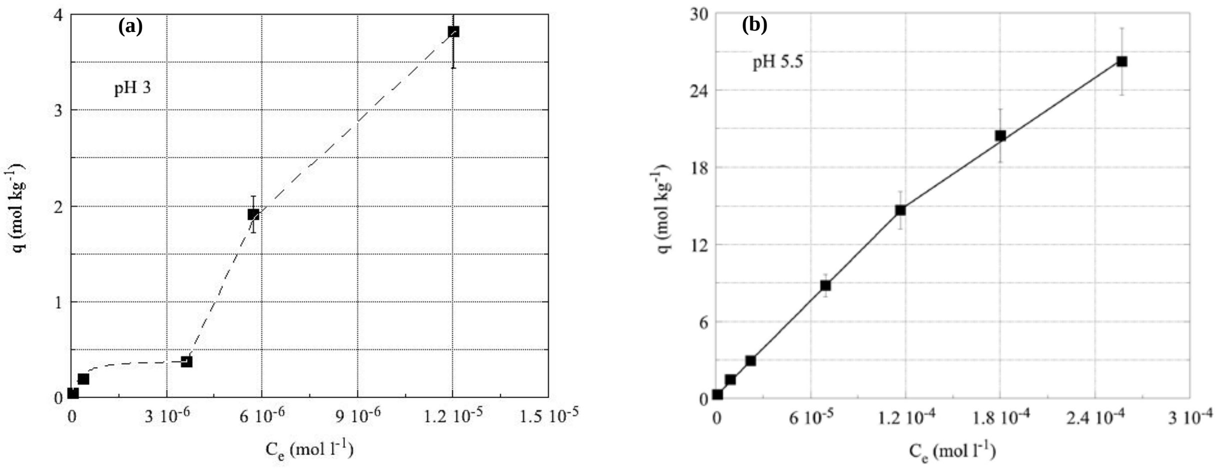


Figure 6. Adsorption isotherms of the U(VI) sorption on activated biochar at **(a)** pH 3 and **(b)** pH 5.5 (0.01 g of biochar, $[U(VI)]_o = 1\cdot10^{-5}$ - $9\cdot10^{-3}$ mol·L^{-1}, I = 0.1 mol·L^{-1} $NaClO_4$, T = 23 ± 2 ^oC, 24 h of reaction time).

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In addition, according to the kinetic data, which were conducted at both pH 3 and pH 5.5, equilibrium occurs within the first 40 and 10 minutes, respectively.

3.2.3 Effect of temperature

The effect of temperature on U(VI) sorption on the activated biochar *Luffa cylindrica* fibres was investigated to estimate the corresponding thermodynamic data based on the linear form of the Van't Hoff equation [6]. Evaluation of the data revealed that the thermodynamic of U(VI) adsorption on activated biochar is different at the two pH regions (Figure 7). Moreover, the sorption is favoured with decreasing temperature (exothermic process, ΔH^o= -0.4 kJ·mol^{-1}; ΔS^o= 87.3 J·K^{-1}·mol^{-1}) at pH 5.5, while, at pH 3 U(VI) adsorption seems to be an endothermic process (ΔH^o= 5.1 kJ·mol^{-1}; ΔS^o= 103.9 J·K^{-1}·mol^{-1}). Therefore, indicating that the sorption mechanisms in the two pH regions are slightly different. Nevertheless, in both cases entropy is the driving force for uranium adsorption by the biochar fibres.

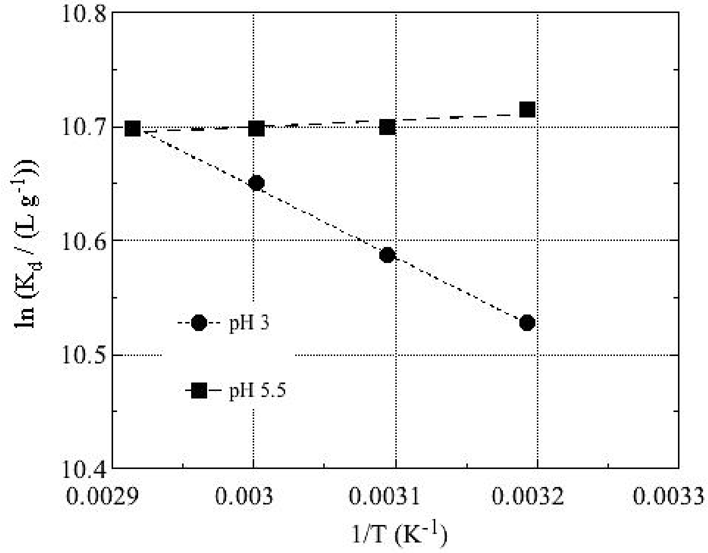


Figure 7. lnK_d as a function of temperature corresponding to U(VI) sorption on activated biochar at pH 3 and pH 5.5 (0.01 g of biochar, $[U(VI)]_o = 5\cdot10^{-4}$ mol·L^{-1}, I = 0.1 mol·L^{-1} $NaClO_4$, 24 h of reaction time).

3.2.4 Effect of ionic strength

Furthermore, the effect of ionic strength on the relative sorption of U(VI) was investigated, in order to understand the interaction mechanisms between U(VI) and the surface functional groups of the bio-sorbent, at pH 3 and pH 5.5. According to the experimental data presented in Figure 8, the relative sorption of U(VI) is almost not affected by increasing salinity at both the pH regions, indicating specific interactions between U(VI) and the surface carboxyl groups. The specific interactions could be attributed to the predominance of inner-sphere complexes [14]. This is in agreement with the FTIR results.

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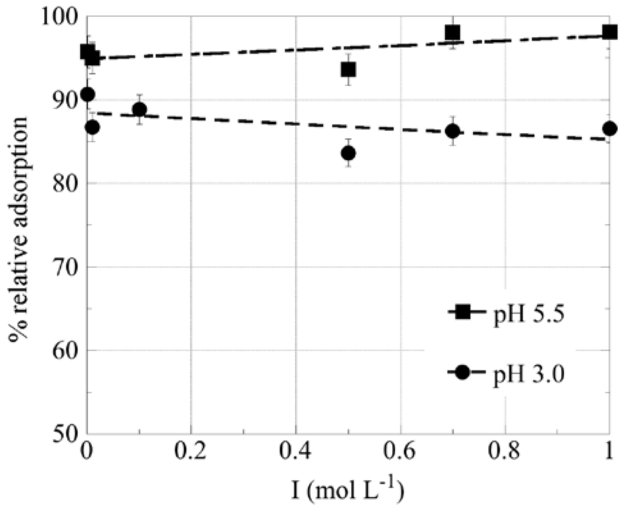


Figure 8. % relative adsorption as a function of ionic strength corresponding to U(VI) adsorption on activated biochar at pH 3 and pH 5.5 (0.01 g of biochar, $[U(VI)]_o = 5 \cdot 10^{-4}$ mol·L^{1}, I = 0.1 mol·L^{-1} $NaClO_4$, T = 23 ± 2 ^oC, 24 h of reaction time).

4. CONCLUSIONS

In this study, activated biochar produced from *Luffa cylindrica* fibres has been used to remove U(VI) from aqueous solutions. The results indicate that the material presents high sorption capacity even in acidic solutions (q_{max}= 92 g·kg^{-1}, at pH 3) and increased chemical affinity for U(VI), which is attributed to the fibrous vascular system of *Luffa cylindrica* and the carboxylic moieties present on the surface. FTIR spectroscopic measurements, as well as effect of ionic strength results prove the formation of inner-sphere complexes between the carboxylic surface moieties and U(VI). The material could be a very attractive candidate for the effective removal of uranium from natural waters (e.g. seawater) and heavily contaminated industrial wastewaters.

References

[1] Choppin G.R., 2007. Actinide speciation in the environment. *Journal of Radioanalytical and Nuclear Chemistry*, **273(3)**, 695-703.
[2] Mishra S., Dwivedi J., Kumar A., Sankararamakrishnan N., 2015. Studies on salophen anchored micro/meso porous activated carbon fibres for the removal and recovery of uranium. *RSC Advances*, **5(42)**, 33023-33036.
[3] Burkart W., Danesi P.R., Hendry J.H., 2005. Properties, use and health effects of depleted uranium. *International Congress Series*, **1276**, 133-136.
[4] Mazali I.O., Alves O.L., 2005. Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (Luffa cylindrica). *Anais da Academia Brasileira de Ciências* **77(1)**, 25-31.
[5] Khan M.H., Warwick P., Evans N., 2006. Spectrophotometric determination of uranium with arsenazo-III in perchloric acid. *Chemosphere*, **63(7)**, 1165-1169.
[6] Atkins P., De Paula J., 2010. *Physical Chemistry*, Oxford University Press, UK.
[7] Chen X., Chen G., Chen L., Chen Y., Lehmann J., McBride M.B., Hay A.G., 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*, **102(19)**, 8877-8884.
[8] Wruck D.A., Brachmann A., Sylwester E.R., Allen P.G., Palmer C.E.A., 1999. Sorption of Np(V) by U(W) Hydroxide Solids UCRL-JC-135791. Livermore, California: Lawrence Livermore National Laboratory.
[9] Baes C.F., Mesmer R.E., 1976. *The Hydrolysis of Cations*, Wiley, New York.
[10] Pashalidis I., Buckau G., 2007. U(VI) mono-hydroxo humate complexation. *Journal of Radioanalytical and Nuclear Chemistry*, **273(2)**, 315-322.
[11] Zhang Z., Helms G., Clark S.B., Tian G., Zanonato P., Rao L., 2009. Complexation of uranium (VI) by gluconate in acidic solutions: a thermodynamic study with structural analysis. *Inorganic Chemistry*, **48(8)**, 3814-3824.

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[12] Maher K., Bargar J.R., Brown Jr. G.E., 2012. Environmental speciation of actinides. *Inorganic Chemistry*, **52(7)**, 3510-3532.
[13] Prodromou M., Pashalidis I., 2013. Copper (II) removal from aqueous solutions by adsorption on non-treated and chemically modified cactus fibres. *Water Science & Technology*, **68(11)**, 2497-2504.
[14] Prodromou M., Pashalidis I., 2013. Uranium adsorption by non-treated and chemically modified cactus fibres in aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry*, **298(3)**, 1587-1595.
[15] Ai L., Luo X., Lin X., Zhang S., 2013. Biosorption behaviors of uranium (VI) from aqueous solution by sunflower straw and insights of binding mechanism. *Journal of Radioanalytical and Nuclear Chemistry*, **298(3)**, 1823-1834.
[16] Caccin M., Giacobbo F., Da Ros M., Besozzi L., Mariani M., 2013. Adsorption of uranium, cesium and strontium onto coconut shell activated carbon. *Journal of Radioanalytical and Nuclear Chemistry*, **297(1)**, 9-18.
[17] Demir H., Top A., Balkose D., Ulku S., 2008. Dye adsorption behavior of Luffa cylindrica fibers. *Journal of Hazardous Materials*, **153(1)**, 389-394.

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Toxicity assessment of fur-suede processing wastewater treated with different coagulants

G. Yildiz Tore[*], G. Kaykıoğlu

Department of Environmental Engineering, Namık Kemal University, 59860, Çorlu, Tekirdağ,Turkey.
*Corresponding author: Email: gyildiztore@nku.edu.tr

Abstract

There are limited experimental research about the toxicity effect assessment of chemically treated fur-suede processing wastewater. So, the aim of this study to determine the toxic effect of chemicaly treated fur-suede processing wastewater both discharged on receiving bodies and treated later in biological treatment processes. Toxicity assessment were done using with Daphnia magna standart test. 3 different conventional coagulants (FeCl3, Al2SO4, FeSO4) were used for jar test experiments and optimum conditions were determined according to COD and Color removal efficiencies. The results indicated that while the highest and the lowest COD removal efficiencies were obtained from Al2SO4 and FeCl3 treatability experiments as 86,3% and 67,2 % respectively, the highest color removal efficiencies were found as 98% and the best toxicity removal was found 60% for 50% diluted samples obtained from Al2SO4 treatability experiments. These results show that chemical coagulation flocculation as a first treatment step for treatment of fur-suede processing wastewater provide a good performance both to remove particulate material and other pollutants which inhibits biological treatment and also has toxic effect for the receiving bodies.

Keywords: fur-suede wastewater; tannery effluent; daphnia magna toxicity; coagulant; COD and color removal

1. INTRODUCTION

Tannery effluent including fur-suede processes is one of the most difficult industrial wastewaters in terms of treatability characteristics. Furthermore, large amount of freshwater is used to treat leather depending on the processes involved, the raw material used and the manufactured products, and many potentially dangerous chemicals such as chromium, synthetic tannins, oils, resins, biocides, detergents, are released [1;2]. By the way, fur-suede processing wastewaters also exhibit a strong wastewater characteristics with a maximum total COD of around 4285 mg/l, despite the excessive water usage of more than 200 m^3 per ton of skin processed. The first six processes including washing, pickling and bating steps had the highest impact on the plant effluent, contributing 40% of the flow and more than 50% of the COD load together with significant amounts of trivalent chromium, sulphide and chloride often inducing inhibitory or toxic impact on biological treatment processes [3-5]. So, ideally, chromium and sulfide line waste streams are separated and they are pre-treated for chromium and sulfide removal by coagulation/flocculation and catalytic oxidation processes, respectively [6]. Because, chemical treatments have also been shown to be effective in removing these inhibitors [7]. Aluminium and ferric salts are widely used as coagulants in water and wastewater treatment and in some other applications [8]. Both chromium and sulfide waste streams are then mixed to decrease BOD and COD contents via conventional biological treatment [9]ç On the other hand, various physico-chemical techniques have been studied for their applicability to the treatment of tannery wastewater [10;11]. But there are limited studies to

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optimise the operating conditions for coagulation of tannery wastewaters. The efficiency of Coagulation-Floculation (CF) is mainly influenced by raw wastewater characteristics, pH, temperature, coagulant type and dose and mixing velocity [12].

The another most important concerns related to effluents originated from this industry are mainly due to chronic toxic effects caused by the mixture of many compounds used in the process that can be released to the environment because they even remain after conventional treatment [13;14]. Individual components such as phenols, formaldehyde are persisting conventional chemical and/or biological wastewater treatment processes [15]. The effect of chromium on biological treatment efficiency has been studied in detail [16], however, during tanning process some chemicals such as fungicides, synthetic tannins, dyes, surfactants are also used which have been indicated to inhibit the biological nitrification [17] and are toxic to aquatic environment [18-20] tested on different bioassays including Vibrio fisheri [21], Daphnia magna [22], sea urchins and marine microalgae [23]. The toxicity tests are useful analytical tools for screening of chemical analysis and as an early warning system to monitor the treatment of WWTPs. The use of single toxicity test or battery of tests is the best approach to evaluate the risk because they are reliable indices of the toxic impact of effluents in the aquatic environment [24]. The use of Daphnia magna in toxicology is accepted in several countries to monitor wastewater treatment systems, to establish quality criteria to determine permissible concentrations of pollutants, limits of impurity in water from natural effluents, and to determine the efficiency of a good sanitation method [25]. A number of toxicity monitoring and removal studies have been performed on leather tanning wastewater including acute toxicity on Vibrio fisheri , Daphnia magna [21; 22;26].

So, since there is limited information in the literature for evaluation of wastewaters associated with different production categories of tannery influents and also for fur-suede effluents, this study is intended to fill this gap and provides original information on the toxicity assesment of fur-suede processing wastewater treated with different coagulants . So, this paper firstly evaluates the experimental study results that were conducted on raw wastewater occurred from fur-suede production in terms of coagulation efficiencies based on COD, SS and colour removal at various pH and coagulant doses with regard to pre-treatment standards. After the optimum conditions were described for coagulation, chemically treated wastwaters' toxicity which inhibits biological treatment and also affects receiving bodies negatively was evaluated.

2. MATERIALS AND METHODS

2.1. Wastewater, sampling and conservation

The investigated leather plant, located in the Çorlu Leather Organized Industrial District in Tekirdağ-western part of Turkey, was selected for the study. It processes sheep and lamb skins to give fur-suede and works five days a week with two shifts a day, employing a total of 140 people. The capacity of the plant is 2400 tons of skins per year, corresponding to around 6.4 tons of skin per day. Skins are processed using paddles and mixers of different capacity, varying between 6 and 32 tons. Based on wastewater management, the plant can be classified in subcategory IV – shearlings or in subcategory VI – sheepskin for suede, based on the classification proposed by Tünay et al.[27. In district, most of the plants work on sem-pickled and fur-suede leather tanning. Occured wastewaters from these plants were treated at Çorlu Leather Organised WWTP receiving an inflow of 36,000 $m^3.d^{-1}$, and consisting of an equalization basin followed by a coagulation and flocculation process and biological nitrification. Experimental studies were carried out fur-suede plant effluent samples characterized along with 1 month. Samples were delivered to the laboratory in 1 h for chemical analysis and acute toxicity tests and kept refrigerated at +4 ^{0}C during analysis.

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2.2. Jar tests procedure

A series of Jar-test experiments were performed on raw wastewater applying 2 min rapid mixing (RM) at 100 rpm, 20 min slow mixing (SM) at 30 rpm and 30 min settling at different pH values and coagulant dosages . Aluminium sulphate [$Al_2 (SO_4)_3.18H_2O$], ferric chloride [$FeCl_3 .6H_2O$] and ferrous sulfate [$FeSO_4.7H_2O$] were used as coagulant. Solid Anionic Polyelectrolyte was supplied from Zhengzhou Jing Lian Water Purification Materials Co., Ltd. (Henan, China, polyacrlamide based, 99% purity). All chemicals used in this study were analytical reagent grade.A conventional Jar–test apparatus (VELP Scientifica, FC6S) equipped with four beakers with 1000 ml were used. These compounds were purchased from Merck chemicals. After settling, supernatant samples were collected and filtered using coarse filter (Whatman filter paper no.40.) for further analysis. Jar test trials were made at efficient pH (8,5 for alum, 9,5 for ferrous sulphate and 10 for ferric chloride by adding 1N HCl or 1 N NaOH solutions) and different flocculant dosages (200, 400, 600, 800 $mg.L^{-1}$). Optimum conditions were assesed for Colour, COD and SS removal. All experiments were performed at room temperature (20- 25 ^0C).

2.3. Analytical Methods

All analyses were performed according to the Standard Methods [28;29] and ISO 7887 method [30]. The adjustment and measurement of pH was carried out using a (WTW pH315i) pH meter.

2.4. Toxicity-Daphnia magna

The toxicity of raw and coagulated wastewater was measured using 24 h *Daphina Magna* with and without and 50% dilution [31] to evaluate the influence of wastewater characteristics. For instance, there was found a positive relation between conductivity and juvenile daphnids mortality [32] while over 25 $mg.L^{-1}$ ammonia exhibited 50% of immobilization of daphnids [33]. Toxicity tests were performed quadruplicate using 5 daphnids in each test beaker with 100 ml effective volume. New born daphnids were grown in the laboratory at 16 h day light and 8 h dark periods supplying a 3000 lux illumination. They were fed with Selenastrum capricornutum (300.000 cells ml^{-1}) and baker's yeast (Schizosaccharomyces cerevisiae, 200.000 cells ml^{-1}). Room temperature was kept at $20^oC \pm 1^oC$ and a minimum 6 mg l-1 of dissolved oxygen was supplied by air filtered through activated carbon. All solutions were prepared using bi-distilled water at pH 8.0. Results were expressed as a percentage of immobilised animals after 24 h and 48 h.

3. RESULTS AND DISCUSSION

3.1. Effluent Characterization

Wastewater characterization of investigated plant used in jar test experiments is given Table 1.

All the striking features in Table 1 presents a typical tannery wastewater characteristics and shows a complex and strong wastewater structure especially with total COD about 1975 mg. L-1 and . The suspended solids (SS), Total azot (T-N), colour, conductivity and total chromium (Tot-Cr) concentrations. The effluent characteristics associated with the plant are representative of the leather tanning wastewater and agree approximately with the values reported in the literature [benim makalem, 8,23,24].

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Table 1. Wastewater characterization of investigated plant used in jar test experiments

PARAMETERS	UNIT	Raw WW
Total COD	mg.L^{-1}	1975$\pm$ 12
Total TOC	mg.L^{-1}	340$\pm$3
Soluble TOC	mg.L^{-1}	188$\pm$13
Suspended Solid (SS)	mg.L^{-1}	560 $\pm$6
Conductivity	µmho.cm^{-1}	7930$\pm$123
Colour 436 nm	CN*(m^{-1})	74,5
525 nm	CN*(m^{-1})	55,7
620 nm	CN*(m^{-1})	44,4
Total Cr (T-Cr as Cr+3)	mg.L^{-1}	55$\pm$7,3
T-N	mg.L^{-1}	
Soluble T-N	mg.L^{-1}	29$\pm$1,7
	mg.L^{-1}	19$\pm$2,3
pH	-	5,65$\pm$0,7

*CN: Colour number

3.2. Optimisation of the coagulant dose and the performance in the coagulation/floculation process

Three different coagulants and four different dosages were used for optimisation of treatability conditions for fur-suede raw wastewater at coagulation/flocculation process. The results is given at Table 2.

Table 2. Treatability results of fur-suede raw wastewater

SETS	Coagulant	Dosage mg.L-1	pH	COD mg.L-1	TSS mg.L-1	TOC mg.L-1	T-N mg.L-1	Conductivity µS/cm	COLOUR (Colour Number, m^{-1}) (436 nm)	(525 nm)	(620 nm)
SET-1	FeCl3 (10%)										
Set-1.1		200	10	1261	135	206,5	28,37	8560	11,8	7,1	4,5
Set-1.2		400	10	687	80	216,8	29,45	9160	3,4	2,3	1,4
Set-1.3		600	10	556	85	*	24,18	9680	3,8	2,7	2,1
Set-1.4		800	10	647	95	211,6	30,28	9930	4,1	2,9	2,4
SET-2	FeSO4 (10%)										
Set-2.1		200	9,5	1363	640	305,1	32,44	8100	73,4	46,5	34,9
Set-2.2		400	9,5	1177	490	260,9	34,27	8190	49,5	28,9	20,5
Set-2.3		600	9,5	485	320	216,2	38,19	8210	40,4	21,7	14,1
Set-2.4		800	9,5	417	85	214,1	37,25	8460	3,3	2,5	1,5
SET-3	Al2(SO4)3 (10%)										
Set-3.1		200	8,5	1250	700	286,3	35,55	8350	111,3	88,2	76,1
Set-3.2		400	8,5	1206	520	218,7	34,64	8390	60,2	40,7	30,9
Set-3.3		600	8,5	657	165	161,9	36,25	8420	18,7	12,7	9,5
Set-3.4		800	8,5	270	60	143,7	36,9	8600	1,8	1	0,3

According to the Table 2, it was observed that colour removal increased with the increasing $FeCl_3$ concentration. Colour removal was determined as 87% at 200 mg.L^{-1} $FeCl_3$ dosage while it was found 96% at 400 mg.L^{-1} at pH=10. The worst colour removal in this study occurred at the lowest dose. Dosage amount increased to begin the colour removal efficiency increase and reached close to each other. On the other hand, $FeSO_4$ and $Al_2(SO_4)_3$ experiments showed that the meaningful colour removal efficiency can be obtained at 800 mg.L^{-1} concentration as 96% and 98%, respectively. So, in this case, according to the colour removal efficiency results, since $FeSO_4$ and $FeCl_3$didn't present a good performance even at very high concentrations compared to $Al_2(SO_4)_3$ and were found more expensive option, $Al_2(SO_4)_3$ was assessed the best coagulant which provide the best colour removal efficiency for this wastewater. Moreover, COD removal

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efficiencies were increased with increasing $FeCl_3$ concentration similar to the colour removal. When $FeCl_3$ concentration increased from 200 $mg.L^{-1}$ to 800 $mg.L^{-1}$, COD removal increased from 36% to 67%. But the best COD removal efficiency was achieved as 72% at 600 $mg.L^{-1}$ $FeCl_3$ dosage and pH=9,5. $FeSO_4$ and $Al_2(SO_4)_3$ coagulants were also showed the similar intend. COD removal efficiency 31% at 200 $mg.L^{-1}$ $FeSO_4$ dosage and pH=8,5, while it was found 96% at 800 $mg.L^{-1}$ for the same pH. On the other hand, when $Al_2(SO_4)_3$ dosages were increased from 200 $mg.L^{-1}$ to 800 $mg.L^{-1}$, COD removal increased from 37% to 86 at pH=8,5 %. When TSS analysis were assessed, the best TSS removal efficiencies were determined as 86% for 400 $mg.L^{-1}$ $FeCl_3$ dosage at pH=10, 85% for 800 $mg.L^{-1}$ $FeSO_4$ dosage at pH=9,5 and 89% for 800 $mg.L^{-1}$ $Al_2(SO_4)_3$ at pH=8,5.

As a conclusion, in terms of COD and TSS removal efficiencies, for optimum dosages of $FeCl_3$ (600 $mg.L^{-1}$), $FeSO_4$ (800 $mg.L^{-1}$) and $Al_2(SO_4)_3$ (800 $mg.L^{-1}$) were determined as 77 %, %79, %86, respectively. By the way, TSS removal efficiencies for them were calculated as 86%, 85% and 89 %, respectively. So, in this case, according to the chemical settling experiment results, since $FeSO_4$ and $FeCl_3$ didn't present a good performance even at very high concentrations compared to $Al_2(SO_4)_3$ especially for COD and TSS removal and were found more expensive option, $Al_2(SO_4)_3$ was assessed the best coagulant which provide the best removal efficiency for this wastewater. Song et.al. (2000) found at an optimum pH of 7.5, the following removal efficiencies were attained by coagulation: 32%±35.6% (COD), 64.0%±69.3% (SS), 77±99% (chromium), 85%±86% (colour) by respectively the addition of 800mg l±1 of aluminium sulphate or ferric chloride [34]). Furthermore, Song et al. (2004) obtained a removal range of 30–37% of total COD, 74–99% of chromium and 38–46% of SS using 800 mgL−1of alum at 7.5 pH for pre-settled tannery wastewater containing 260 mgL−1 of SS, 16.8 mgL−1 of chromium, 3300 $mg.L^{-1}$of COD at pH 9.2. [35]. So, the COD and TSS removal efficiencies were reported more lower than this study results. Furthermore, they reported that $FeCl_3$ proved better results than alum. Ates et al. (1997) investigated the effectiveness of alum and $FeCl_3$ based-CF for the treatment of homogenized inlet of a central treatment plant of leather tanneries district, Turkey. All experiments resulted in >70% of COD removal [36]. Total chromium was also effectively (5 $mg.L^{-1}$) removed by alum while it was almost completely removed using $FeCl_3$. Kabdasli et al. (1999) also reported 40–70% removal of COD and >99% of total chromium from leather tanning wastewater using $FeSO_4$, $FeCl_3$ and alum [37]. So, this study results showed the best removal efficiencies in terms of COD and TSS parameters compared to the literature. It is tought that the reason of this is due to the the weak character of fur--suede wastewater used in this study unlike the literature.

3.3. Toxicity-Daphnia magna

The toxicity of raw and coagulated wastewater at optimum coagulant dosages (**Set 1-3:** $FeCl_3$ - 600 $mg.L^{-1}$ at pH=10, **Set 2-4:** $FeSO_4$ -800 $mg.L^{-1}$at pH=9,5 and **Set 3-4:** $Al_2(SO_4)_3$ -800 $mg.L^{-1}$ at pH=8,5) were measured using 24 h *Daphina Magna* with and without 50% dilution to evaluate the influence of wastewater characteristics in the scope of 3 sets. The results are given at Table 3. *Daphnia Magnas* didn't show a good vitality at also 24 h. So, when 48 h effects were considered, it was observed that all of the *Daphnia Magnas'* were died. The meaning of this can be explained that while there is most important toxicity at acute period, this case will result in high toxicity at long period.

According to the toxicity tests, all *Daphnia Magnas* were died without dilution. But, it was obtained that a chancing specific toxicity was removed according to the different coagulants. On the other hand, dilution had a possitive effect on toxicity compared to the undiluted raw samples. The reason of the high toxicity of raw wastewater is due to the untreated. Furthermore, high COD, TSS, Conductivity of raw wastewater may be reason for this case. But,experimental results show that although raw wastewater is untreated, it was observed that a specific volume of dilution provide approximately 10% $\pm$ 3 toxicity removal. On the other hand, toxicity of chemically coagulated

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Table 3. The toxicity evaluation of raw and coagulated fur-suede wastewater

SAMPLE NAME	50% Diluted wastewater Immobilisation *Daphina Magna* number, 24 h At the beginning of experiment	Mortality	Vitality	Average toxicity (%)
Set-1				
Control	5	0	5	0
Raw wastewater	5	4	1	80
Set 1-3 ($FeCl_3$ -600 mg.L^{-1} at pH=10)	5	3	2	60
Set 2-4 ($FeSO_4$ -800 mg.L^{-1}at pH=9,5)	5	4	1	80
Set 3-4 ($Al_2(SO_4)_3$ -800 mg.L^{-1} at pH=8,5)	5	2	3	40
Set-2				
Control	5	0	5	0
Raw wastewater	5	5	0	100
Set 1-3 ($FeCl_3$ -600 mg.L^{-1} at pH=10)	5	4	1	80
Set 2-4 ($FeSO_4$ -800 mg.L^{-1}at pH=9,5)	5	3	2	60
Set 3-4 ($Al_2(SO_4)_3$ -800 mg.L^{-1} at pH=8,5)	5	2	3	40
Set-3				
Control	5	0	5	0
Raw wastewater	5	4	1	80
Set 1-3 ($FeCl_3$ -600 mg.L^{-1} at pH=10)	5	4	1	80
Set 2-4 ($FeSO_4$ -800 mg.L^{-1}at pH=9,5)	5	3	2	60
Set 3-4 ($Al_2(SO_4)_3$ -800 mg.L^{-1} at pH=8,5)	5	2	3	40

wastewater diluted with 50% were calculated averagely as 70±5% for $FeCl_3$ and provided best toxicity removal as 20% at Set 1-3. At this set, it was observed that the shape of the immobilised *Daphnia Magnas* were broken. But unlike this situation, they were maintained their transparent colour during this period. Furthermore, toxicity of Set 2-4 was determined averagely as 60±7%, toxicity removal was found approximately 40% and it was observed that *Daphnia Magna*s didn't protect their shape and with degradation, theri colour converted to a salmon colour. It is thought that both the acidic properties of coagulant used in this set and $SO_4^{=}$ and Fe ion affects at high dosages may be the reason of the toxicity. On teh other hand, the highest toxicity removal was achieved at Set 3-4 with alum. Averagely, 40% toxicity was determined for alum coagulant at 50 % dilution and 60% toxicity removal was achieved. The reason of this can be explained as the highest coagulation efficiencies can be achieved with alum coagulant on the base of high COD, TSS and Colour removal. By the way, it was reported in the literatüre that the toxic effect of aluminium ions have lower affect on the aqualife than iron ions. It was thought that this case may also has a possitive effect on a little bit lower toxiciy. In the literatüre, Kaptan, D.(2002) was researched the acute *Daphnia Magna* toxicity of textile wastewater and found that while the raw textile wastewater 100% toxic with 50% dilution, the toxicity of wastewater treatment plant effluent treated this raw wastewater was determined 20% toxic with 50% dilution. Lofrano et.al. also studied leather tanning wastewater *Daphnia Magna* toxicity at severeal researchs. The also found that the overall decrease in effluent toxicity following the coagulation/floculation effluent suggested an effective removal of toxic components from tannery wastewater [38]. So, it is useful approach to improve the coagulation process for toxicity reduction of raw wastewater taken from a leather tanning wastewater. This study results showed that to improve COD and TSS removal as well reduce the toxicity of the existing coagulation/floculation treatment process may be useful to remove of toxic components from fur-suede wastewater before both biological treatment and discharge to receiving bodies. Especially, the policy of submitting tannery wastewater to biological treatment before its release in receiving water bodies is necessary to reduce toxicity using alum coagulation for protecting the aquatic environment.

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4. CONCLUSIONS

This study aimed to optimize pH and coagulant dosage for the wastewater originated from a fur-suede process to improve coagulation efficiency as well reduce the toxicity of it. Toxicity was monitored in raw and coagulated samples using *Daphnia Magna* test. The optimum conditions were assessed as 8.5 pH and 800 mg.L^{-1} of $Al_2(SO_4)_3$ with the pH adjustment by using $Ca(OH)_2$ which resulted in high removal of COD (86 %), TSS(89 %), Colour (98%) and reduced *Daphnia Magna* immobilization (60% v/v toxicity removal). The toxicity tests are useful analytical tools for screening of chemical analysis and as an early warning system to monitor the treatment of WWTPs. The use of single toxicity test or battery of tests is the best approach to evaluate the risk because they are reliable indices of the toxic impact of effluents in the aquatic environment [24]. The coagulation/flocculation process is versatile before submitting the raw tannery effluent to biological process. However, this process must be well optimized to avoid elevated toxicity with respect to raw wastewater and toward the effluent submitted to biological treatment.

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References

[1] Suresh V., Kanthimathi M, Thanikaivelan P, Raghava Rao J, Unni Nair B.,2001. An improved product-process for cleaner chrome tanning in leather processing. *J Clean Prod.*, **9**:483–91.

[2] Nazer, D. W., Al-Sa’ed, R. M., & Siebel, M. A., 2006. Reducing the environmental impact of the unhairing–liming process in the leather tanning industry. *Journal of Cleaner Production*, **14**, 65–74.

[3] G. Yıldız Töre, G. Insel, E.Ubay Çokgör, E. Ferlier, I. Kabdaşlı, D. Orhon, 2011.’’Pollution profile and biodegradation characteristics of fur-suede processing effluents’’, *Environmental Technology*, **32(10)**, 1151-1162,

[4] Lofrano G., Meriç S., Zengin G.E. Orhon D., 2013. ‘’Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review’’, *Science of the Total Environment*, **461-462**, pp. 265-281,

[5] Lofrano G., Aydin E., Russo F., Guida M., Belgiorno V., Meric S., 2008. ‘’Characterization, Fluxes and Toxicity of Leather Tanning Bath Chemicals in a Large Tanning District Area (IT)’’, *Water, Air, & Soil Pollution: Focus*, **Volume 8, Issue 5**, pp.529-542,

[6] Boller, M., 1993. Removal of organic matter by physicochemical mechanism in wastewater treatment plants. *Water Sci. Technol*., **27**, 167–183.

[7] Orhon, D, Ates, E. and Ubay Cokgör, E., 1999, *Wat Envir Res*, **71(1),** 50±63.

[8] Reemtsma, T. and Jekel, M.,1997, *Wat Res,* **31(5),** 1035±1046.

[9] Tiravanti, G., Petruzzelli, D., Passino, R., 1997. Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery. *Water Sci. Technol*. **36**, 197–207.

[10] Amokrane A., Cornel C., Veron J., 1997. Landfill leachates pretreatment by coagulation- flocculation. *Wat. Res.*, **31(11)** 2775-2782.

[11] Orhon D., Sözen S., Ubay Cokgör E. , Ates E., 1998. The effect of chemical settling on the kinetics and design of activated sludge for tannery wastewater. *IAWQ 19th Biennial International Conference*, **998**, pp. 256-363.

[12] Rossini, M., Garrido, J.G., Galluzzo, M., 1999. Optimization of the coagulation-flocculation treatment: Influence of rapid mix parameters, *Wat. Res.,* **33(8),** 1817-1826

[13] Oral R, Meriç S, De Nicola E, Petruzzelli D, Della Rocca C, Pagano G., 2007. Multi-species toxicity evaluation of a chromium-based leather tannery wastewater. *Desalination*, **211**, 48–57.

[14] De Nicola, E., Meriç, S., Della Rocca, C., Gallo, M., Iaccarino, M., Manini, P., et al. 2007a. Wastewater toxicity of tannin- vs. chromium-based leather tanneries in Marrakesh, Morocco. *Archives of Environmental Contamination and Toxicology*, **53(3)**, 321–328.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[15] Lofrano G., Meric S., Belgiorno V., 2007a;. Fenton's oxidation of various based synthetic tannins (syntans). *Desalination*, **211,** 10–21, Napoli RMA.
[16] Orhon D., Genceli E.A., Cokgor E.U., 1999. Characterisation and modelling of activated sludge for tannery wastewater. *Wat. Environ. Res.*, **71**, 50– 63.
[17] Jochimsen J.C., Jekel M.R., 1997. Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. *Wat. Sci. Tech.*, **35,** 337–345.
[18] Banhart J.,1997. Chromium chemistry and implications for environmental fate and toxicity. *J. Soil. Contam.,* **6**, 561–568.
[19] Chattopadhyay B., Gupta R., Chatterjee A., Mukhopadhyay S.K.,, 1999. Characterisation and ecotoxicity of tannery wastes envisaging environmental impact assessment. J. Am. *Leather Chemist Assn.,* **94,** 337–346.
[20] Klinkow N., Oleksy-Frenzel J., Jekel, M., 1998. Toxicity-directed fractionation of organic compounds in tannery wastewater with regard to their molecular weight and polarity. *Wat. Res.*, **32,**2583–2592.
[21] Jochimsen, J.C., Jekel, M.R., 1997. Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. *Water Sci. Technol.* **35**, 337–345.
[22] Tisler T., Zagorc-Koncan J., Cotman M., Drolc A., 2004. Toxicity potential of disinfection agent in tannery wastewater. Water Res., **38,** 3503– 3510.
[23] Nicola E. De, Gallo M., Iaccarino M., Meriç S., Oral R., Russo T., Sorrentino T., Tünay O. Vutta riello E., Warnau M., Pagano G., 2004. Hormetic vs. toxic effects of vegetable tannin in a multi-test study. *Arch. Environ. Contam. Toxicol.,* **46,** 336–345.
[24] Hernando, MD, Fernandez-Alba, AR, Tauler, R and Barcelo, D., 2005. Toxicity assays applied to wastewater treatment, Talanta **65**, 358- 366.
[25] Villegas- Navarro, A , Romero Gonzalez, MC and Rosas Lopez, E., 1999. Evaluation of Daphnia magna as an indicator of toxicity and treatment efficacy of textile wastewater. *Environmental International*, **25**, 619- 624.
[26] Oral R., Russo T., Sorrentino T., Tünay O., Vuttariello E., Warnau M., Pagano G., (2004). Hormetic vs. toxic effects of vegetable tannin in a multi-test study. Arch. *Environ. Contam. Toxicol,* **46**, 336-345
[27] Tünay O., Kabdaşlı I., Orhon D., Ateş E., 1995. Characterization and pollution profile of leather tanning industry in Turkey, Water Sci. Technol. **32** , pp. 1–9.
[28] Standard Methods for the Examination of Water and Wastewater, 1998. 20th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA
[29] ISO 6060, 1986. Water Quality−Determination of the Chemical Oxygen Demand, Reference No: 6060−1986.
[30] ISO 7887, 1994. Water quality-determination of color, International Organization for Standardization, Ref. No. ISO 7887, 1994 (E), Switzerland.
[31] ISO, 1996. Water quality: determination of the inhibition of the mobility of Daphnia Magna Starus (cladocera, Crustacea)- Acute toxicity test, ISO(International Organisation for Standardisation, Geneva, Switzerland) 66431
[32] Villegas-Navarro, A., Ramiez,-M.Y., Salvador, M.S., Gallardo, J.M., 2001. Determination of wastewater LC50 of the different process stages of the textile industry, *Ecotox. Environ. Saf.,* **48**, 56-61.
[33] Marttinen, S.K., Kettunen, R.H., Sormunen, K.M., Soimasuo, R.M., Rintala, J.A., 2002. Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates, *Chemosphere*, **46**, 851-858
[34] Song Z., Williams C. J., R. G. J. Edyvean, 2001. Coagulation And Anaerobic Digestion Of Tannery Wastewater Trans, *IChemE*, Vol **79**, Part B.
[35] Song Z, Williams CJ, Edyvean RGJ. 2004 Treatment of tannery wastewater by chemical coagulation.*Desalination*, **164**, 249–59
[36] Ates E, Orhon D, Tunay O., 1997. Characterization of tannery wastewaters for pretreatmentselected case studies. *Water Sci Technol*.,**36**,217–23.
[37] Kabdasli I, Tunay O, Orhon D., 1999. Wastewater control and management in a leather tanning district. *Water Sci Technol*, **40**, 261–7.
[38] Lofrano G., Belgiorno V., Gallo M., Raimo A., Meriç S. 2006. Toxicity reduction in leather tanning wastewater by improved coagulation flocculation process. *Glob Nest J* , **8**,151–8.

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Evaluation of reuse of biologically treated denim washing and dyeing processing wastewater with nanofiltration membrane

G. Kaykioglu*, R. Gürkan, G. Yildiz Töre

Department of Environmental Engineering, Namık Kemal University, 59860, Çorlu, Tekirdağ,Turkey.
*Corresponding author: Email: gkaykioglu@nku.edu.tr

Abstract

The aim of this study was to investigate the reuse possibility in dyeing processes of biologically treated textile wastewater of a local textile factory (denim washing and dyeing) in Tekirdag, Turkey which has COD:350 mgL^{-1}, color:108.9 m^{-1} and conductivity: 2843 μScm^{-1}. For this aim was evaluated the flux and permeate quality as COD, color and conductivity with different nanofiltration (NF) membranes (NP010 and NP030) under various pressures (4, 6, 8 and 10 bar). On the other hand mass transfer coefficients were calculated with Nernst–Planck equation based on experimental results.

The highest flux values were measured as 83.7 L $m^{-2}.h^{-1}$ and 51.8 L $m^{-2}.h^{-1}$ with NP010 and NP030 membranes under 10 bar pressure, while the lowest flux values were determined as 50.3 L $m^{-2}.h^{-1}$ and 22.5 L $m^{-2}.h^{-1}$, respectively. According to analysis results for permeate quality COD: 30 and 20 mgL^{-1}, color 0.51 and 0.41 m^{-1} and conductivity 2190 and 2162 μScm^{-1}were obtained for NP010 and NP030 under 10 bar pressure, respectively. When compared to literature, nanofiltration permeate water was found to be alternative to fresh water in textile wet processing. According to the Nernst–Planck equation, the Bs (mass transfer coefficient) and Rs (overall removal rate) values are obtained. Rs and Bs values were determined as follows: 0.982 and 0.994 for COD, 0.995 and 0.959 for color, 0.295 and 0.3403 for conductivity and 6.79 and 3.38 for COD, 4.90 and 0.54 for color, 27.39 and 15.87 for conductivity, respectively. According to Bs and Rs, NP030 membrane was determined as the most convenient membrane for aerobically pre-treated wastewater.

Keywords: reuse; nanofiltration; textile wastewater ; mass transfer coefficient

1. INTRODUCTION

Reuse of textile industry wastewater is a major issue due increasing water scarcity in recently [1]. Therefore many advanced treatment methods such as adsorption, oxidation are used, especially membrane processes. However pre-treatment process as biological treatment and coagulation/ flocculation is necessary for advanced treatment. In some studies, nanofiltration (NF) membranes after pre-treatment for reuse of textile wastewater has been used [1-6]. Also it has been worked to determine the mass transfer coefficients of NF membranes in various research [7-13]. The mass transfer of NF membranes can be explained by thermodynamics of irreversible processes. The relationship between R (removal efficiency) and J_v (permeate flux) can be determined according to the Nernst-Planck equation. According to this model, R is determined by the following equation [7-9].

$$R = \frac{R_s . J_v}{J_v + B_s} \tag{1}$$

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In this equation (1) R_s and B_s are constants as removal coefficient and mass transfer coefficients, respectively. This constant value is a function of membrane permeability. The equation (2) is obtained with rearranging of equation (1)[7-9].

$$\frac{1}{R} = \frac{1}{R_s} + \frac{B_s}{R_s}.\frac{1}{J_v} \tag{2}$$

In this study, equation (2) is used to determine the Rs and Bs values from 1/R and 1/Jv relationship between [7-9].

Koyuncu et al. (2001) [7] have studied the pilot-scale NF membrane for dye house effluents of textile industry. Permeate conductivity decreased with increasing pressure. To support this, with the mass transfer coefficient accounts, according to Eq. (2), mass transfer coefficient for conductivity was calculated. Kaykioglu et al. (2011)[8] have evaluated in the Nernst–Planck equation for anaerobically and aerobically pre-treated textile wastewaters with membrane experiments obtained permeate flux and removal rate of COD, color and conductivity. Coşkun et al. (2013) [9] have used reverse osmosis for the treatment of olive mill wastewater and have determined mass transfer coefficient for conductivity parameter. In all studies, permeate quality values have decreased with increasing pressure and calculated mass transfer coefficients have confirmed with these values. It is necessary to study more in order to find out the relationship between the removal efficiency and the operating pressure.

In this study, the reuse possibility of biologically treated textile wastewater of a local textile factory (denim washing and dyeing) was investigated in Tekirdag, Turkey. For this aim, the flux and permeate quality as COD, color and conductivity with different nanofiltration (NF) membranes (NP010 and NP030) was evaluated. On the other hand mass transfer coefficients were calculated with Nernst–Planck equation based on experimental results.

2. MATERIALS AND METHODS

2.1 Wastewater origin

In the study, aerobically treatment plant effluent, that is currently available in local textile factory (denim dye and washing) was studied, which has COD: 350 mg/L, color: 108.9 m^{-1} and conductivity: 2843 µS/cm. In this plant, industrial and domestic wastewaters are treated by physical, biological (aerobic) and granule filtration. The capacity of wastewater treatment plant is 1500 m^3/day. Composite sample was taken for 24 hours which was used as feed water in the membrane process.

2.2 Membrane equipment

The membrane system and membrane cell were supplied by Osmonics® Inc. and a GE Sepa™ CF2, respectively. A cartridge filter (10 µm pore size) was used as a pre-filter to remove coarse particulates from the wastewater. All membrane experiments were performed at 25 °C. NF (NP010 and NP030) membranes were used to filtrate aerobically pre-treated textile wastewaters under pressures of 4, 6, 8 and 10 bar. A flat sheet type membrane was used in the experiments. NF membranes supplied by Macrodyn® Nadir. A new membrane sheet was used for each experiment. The characteristics of the membranes were given in Table 1. Membranes were pressurized by distilled water in order to get to the stable flux of the membranes used in experiments. Flowmeter is set at 300 L/h.

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Table 1. Characteristics of nanofiltration membranes

Membrane type	Manufacturer	Meterial	Membrane property	[a]M.O.P., bar	[b]M.O.T., C[o]
NP 010	Macrodyn® Nadir	Polyethersulfone	Hydrophilic	40	95
NP 030	Macrodyn® Nadir	Permanently Polyethersulfone	Hydrophilic	40	95

[a]Maximum operation pressure, [b]Maximum operation temperature

2.3 Analytical methods

COD, color and conductivity were analyzed for aerobically treated effluent and permeate water. They were performed according to ISO 6060 [14], ISO 7887 [15] and Standard Methods [16], respectively. pH and conductivity parameters were determined using WTW pH 315i/set and WTW Cond. 3210 Set 1 brand appliance, respectively. Color was analyzed by using Thermospectronic Aquamate brand spectrophotometer. Membrane performance was expressed as flux and removal efficiency. Permeate flux was determined gravimetrically. The time-dependent flow and pressure values measured in the experiment were calculated as follows;

Flux (Jv, L/m^2.h) = permeate weight in terms of g and in 5 minutes x density of the water / membrane area.

Removal efficiency was determined by the following equation (3).

$$Ro(\%) = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \tag{3}$$

where; R_o, the observed removal efficiency, C_p and C_f represents the concentration of the feed solution and the permeate stream, respectively [1,17,18].

3. RESULTS AND DISCUSSION

3.1 Permeate Flux and Quality

Permeate fluxes were continuously monitored via digital balance connected to a computer. Permeate flux values obtained in different membrane pressure for 60 minutes are shown in Figure1. It can be seen in Figure 1 that permeate fluxes obtained with NP010 are higher than NP030 for all application pressures and increased with increasing pressure. The highest flux values were measured as 83.7 L/m^2.h and 51.8 L/m^2.h with NP010 and NP030 membranes under 10 bar pressure, while the lowest flux values were determined as 50.3 L/m^2.h and 22.5 L/m^2.h, respectively.

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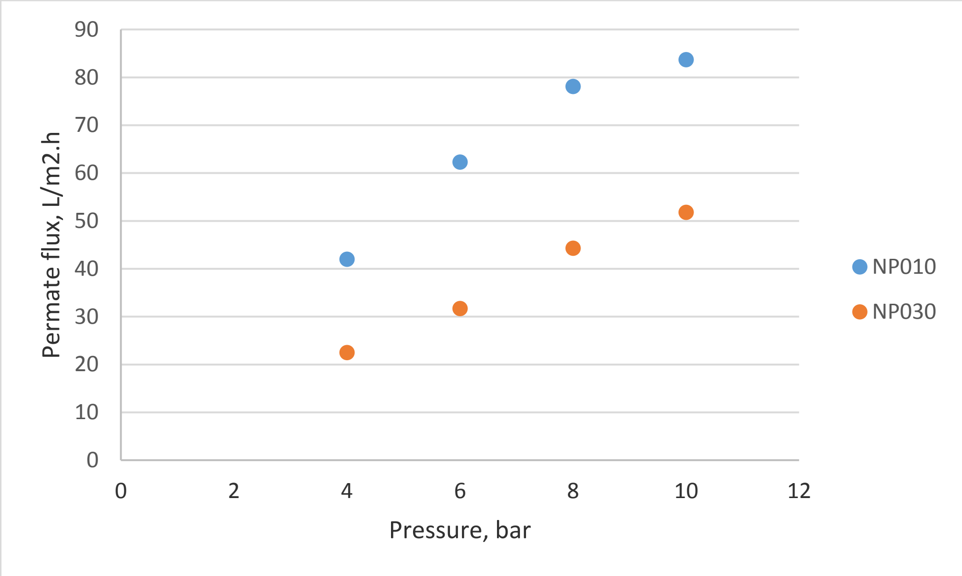


Figure 1. The permeate flux values for NP010 and NP030.

The quality of permeate water obtained (COD, color and conductivity) with NF membranes have been determined to assess of reuse of wastewater (Table 2). The permeate water quality has increased with increasing pressure for all experiments. The permeate waters obtained with NP010 and NP030 have 102-30 mg/L, 11.5-5.1 m^{-1}, 2325-2190 µs/cm and 80-20 mg/L, 6.7-4.1 m^{-1}, 2284-2062 µs/cm for COD, color and conductivity, respectively. Achieved removal efficiencies are shown in Figure 2. It can be seen in Table 2 that permeate waters quality obtained with NP030 is negligibly better than NP010, especially conductivity parameter. According to literature, the industrial process water must have colorless, maximum COD: 50 mg/L and maximum conductivity: 2200 µs/cm [19-21]. If permeate water quality are compared to the results process water quality mentioned in literature, it was proven that obtained permeate waters with NP010 and NP030 under 10 bar can be used in textile industry as a process water.

Table 2. Analysis results of permeate water samples and aerobically pre-treated wastewater

	COD, mg/L	Color, m^{-1}	Conductivity, µs/cm
Aerobically pre-treated wastewater (pH= 6.5)			
	350	108.9	2843
Membrane permeate water			
Pressure, bar	NP010		
4	102	11.5	2325
6	45	9.8	2304
8	32	7.6	2205
10	30	5.1	2190
Pressure, bar	NP030		
4	80	6.7	2284
6	40	6.3	2190
8	28	5.8	2062
10	20	4.1	2162

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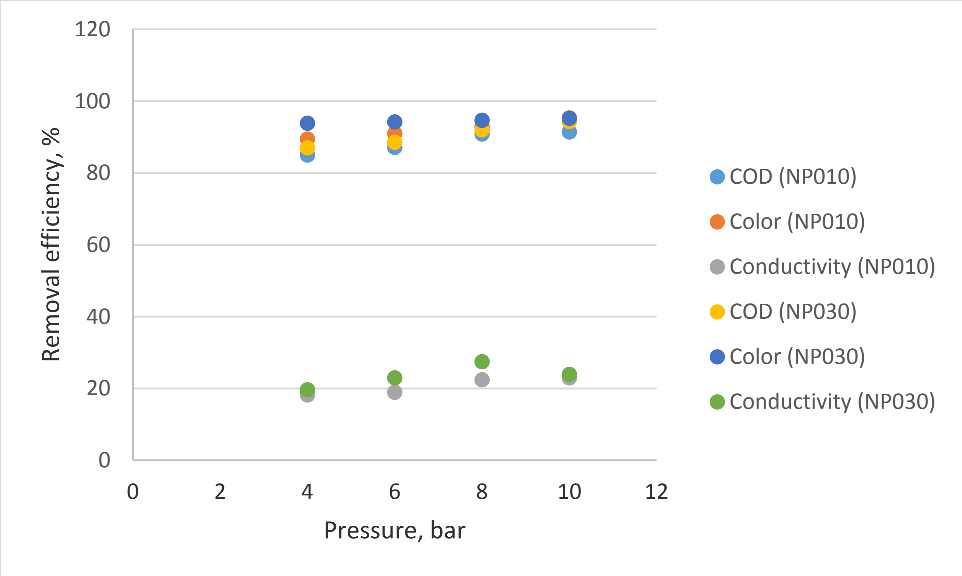


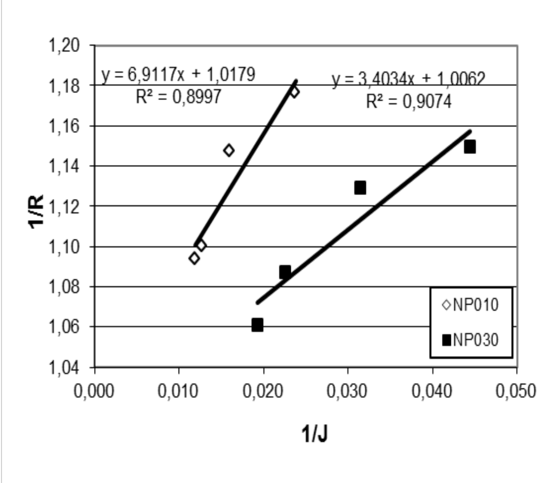
Figure 2. COD, color and conductivity removal efficiencies

3.2 Mass Transfer Coefficiency

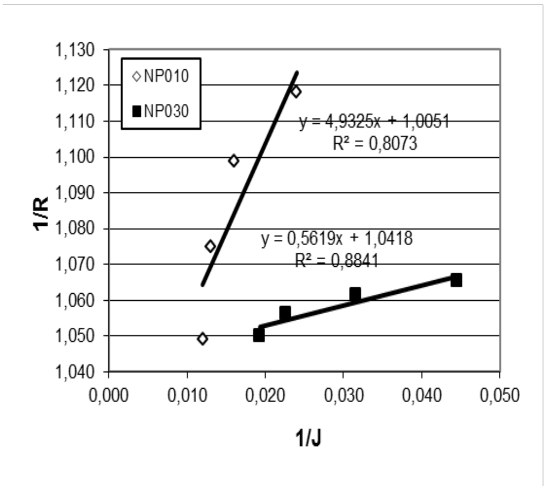
According to the Nernst–Planck equation (Eq.(2)), the Bs (mass transfer coefficient) and Rs (removal coefficient) values are calculated from relationship between 1/Jv and 1/R. The relationships between removal efficiencies (COD, color and conductivity) and permeate flux for aerobically pre-treated wastewaters are given in Figure 3. Bs coefficient indicates passage of the materials through the membrane. Therefore a lower Bs coefficient means higher performance of the membranes.

Rs and Bs values were determined as follows for NP010 and NP030; 0.982 and 0.994 for COD, 0.995 and 0.959 for color, 0.295 and 0.340 for conductivity and 6.79 and 3.38 for COD, 4.90 and 0.54 for color, 27.39 and 15.87 for conductivity, respectively. According to Bs and Rs, NP030 membrane was determined as the most convenient membrane for aerobically pre-treated wastewater due to the fact that Bs values in NP010 were significantly higher than NP030 applications. Kaykioglu et al. (2011) [8] the mass transfer coefficients were determined for aerobically pre-treated wastewater with nanofiltration (NP010 and NP030). Wastewater was supplied from textile factory which dyes 95% of cotton. The Bs coefficiencies of our study were compared with study of Kaykioglu et al. (2011 [8] and the different results obtained (Table 2). According to Kaykioglu et al. (2011) [8], Bs value of conductivity in NP030 membrane was significantly lower than our study. This case can related to the presence of different dissolved organic matter in the effluents due to the different wastewater and treatment mechanisms. The similar results were obtained for COD and color.

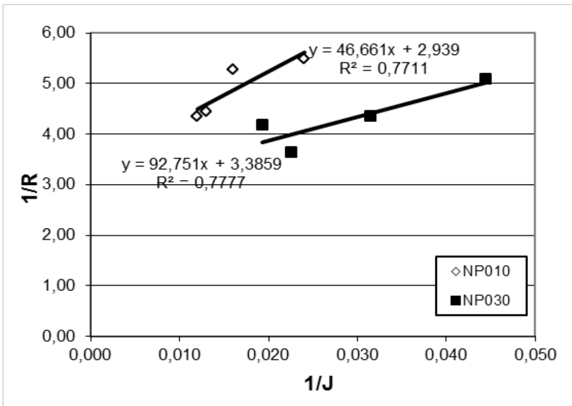
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a)



b)



c)

Figure 3. The relationship between removal efficiency and permeate flux for a) COD, b) color, c) conductivity

Table 2. Bs and Rs values for aerobically pre-treated wastewaters and Bs values of Kaykioglu et al. (2011)[8].

	This study				Kaykioglu et al., 2011 [8]
COD	**R^2**	**Rs**	**Bs/Rs**	**Bs**	**Bs**
NP010	0.8997	0.982	6.9117	6.79	4.99
NP030	0.9074	0.994	3.4034	3.38	1.17
Color					
NP010	0.8073	0.995	4.9250	4.90	0.91
NP030	0.8841	0.959	0.5619	0.54	0.46
Conductivity					
NP010	0.7777	0.295	92.7510	27.39	39.35
NP030	0.7711	0.340	46.6610	15.87	3.06

4. CONCLUSIONS

This study focused on COD, color and conductivity removals from aerobically pre-treated textile wastewater with NF membranes for reuse. Also the performances of NF membranes with their mass

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transfer coefficients were investigated. The highest flux values were measured as 83.7 L/m^2.h and 51.8 L/m^2.h with NP010 and NP030 membranes under 10 bar pressure, respectively. The permeate water quality has increased with increasing pressure for all experiments. According to literature, the permeate waters for NP010 and NP030 under 10 bar pressure can be used in textile industry as a process water. The Bs values in NP010 were significantly higher than NP030 applications. According to Bs coefficiency, NP030 membrane is the most suitable membrane. This case can be explained by difference of membrane materials. NP030 membrane is manufactured from permanently polyethersulfone while NP010 is polyethersulfone. More detailed analyses on the membrane surface are necessary for removal mechanisms.

Acknowledgement

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References

[1] Ellouze, E., Tahri, N., Amar, R.B., 2012. Enhancement of textile wastewater treatment process using Nanofiltration. *Desalination*, **286**, 16–23.

[2] Aouni, A., Fersi, C., Sik Ali, M.B., Dhahbi, M., 2009.Treatment of textile wastewater by hybrid electrocoagulation/nanofiltration process. *J. Hazard. Mater.*, **168**, 868–874.

[3] Bes-Pia, A., Mendoza-Roca, J.A., Alcaina-Miranda, M.I., Iborra-Clar, A., Iborra-Clar, M.I., 2003. Combination of physico-chemical treatment and nanofiltration to reuse wastewater of a printing, dyeing and finishing textile industry. *Desalination*, **157**, 73-80.

[4] Kaykioglu, G., Coban, A., Debik, E., Kayacan, B.B., Koyuncu, I., 2012. The evaluation of fouling effects in membrane process dealing with the biologically pre-treated textile effluents. *Desalination and Water Treatment*, **40**, 1-3.

[5] Debik, E., Kaykioglu, G., Coban, A., Koyuncu, I., 2010. Reuse of anaerobically and aerobically pre-treated textile wastewater by UF and NF membranes. *Desalination*, **256**, 174–180.

[6] Fersi, C., Dhahbi, M., 2008.Treatment of textile plant effluent by ultrafiltration and/or nanofiltration for water reuse. *Desalination*, **222**, 263–271.

[7] Koyuncu, I., Kural, E., Topacık, D., 2001. Pilot Scale Nanofiltration Membrane Separation for Waste Management in Textile Industry.*Water Sci. Technol.*, **43(10),** 233.

[8] Kaykioglu, G., Coban, A., Debik, E., Kayacan, B.B., Koyuncu, I., 2011. Mass transport coefficients of different nanofiltratıon membranes for biologically pre-treated textile wastewaters. *Desalination*, **269**, 254-259.

[9] Coskun, T., Yildirim, A., Balcik, C., Manav Demir, N., Debik, E., 2013. Performances of Reverse Osmosis Membranes for Treatment of Olive Mill Wastewater. *Clean – Soil, Air, Water*, **41 (5)**, 463–468.

[10] Murthy, Z.V.P., Chaudhari, L.B., 2009. Separation of binary heavy metals from aqueous solutions by nanofiltration and characterization of the membrane using Spiegler–Kedem model. *Chemical Engineering Journal*, **150**, 181–187.

[11] Nagy, E., Kulcsár, E., Nagy, A., 2011. Membrane mass transport by nanofiltration: Coupled effect of the polarization and membrane layers. *Journal of Membrane Science*, **368**, 215–222.

[12] Cuartas-Uribe, B., Vincent-Vela, M.C., lvarez-Blanco, S. A´, Alcaina-Miranda, M.I., Soriano-Costa, E., 2007. Nanofiltration of sweet whey and prediction of lactose retention as a function of permeate flux using the Kedem–Spiegler and Donnan Steric Partioning models. *Separation and Purification Technology*, **56**, 38–46.

[13] Al-Zoubi, H., Hilal, N., Darwish, N.A., Mohammad, A.W., 2007. Rejection and modelling of sulphate and potassium salts by nanofiltration membranes: neural network and Spiegler–Kedem model. *Desalination*, **206**, 42–60.

[14] ISO 6060, 2012. Water quality, *Determination of chemical oxygen demand*.

[15] ISO 7887, 2011.Water quality, *Examination and determination of colour*.

[16] APHA, AWWA, and WPCF, 2005. 20th Ed., Washington, DC.

[17] Koyuncu, I., Topacık, D., Yuksel, E., 2004. Reuse of reactive dyehouse wastewater by nanofiltration: process water quality and economical implications. *Separation and Purification Technology*, **36**, 77–85.

[18] Kural, E., 2000. *Recycling and color removal of textile dyeing wastewater with nanofiltration membranes*. Master thesis, Istanbul Technical University, Institute of Natural Science.

[19] Vajnhandl S., Valh J.V., 2014. The status of water reuse in European textile sector. *Journal of Environmental Management*, **141**, 29-35.

[20] Li, X.Z., Zhao, Y.G., 1999. Advanced treatment of dyeing wastewater for reuse. *Water Science and Technology*, **39(10-11),** 249-255.

[21] Marcucci, M., Ciardelli, G., Matteucci, A., Ranieri, L., Russo, M., 2002. Experimental campaigns on textile wastewater for reuse by means of different membrane processes. *Desalination*, **149**, 137–143.

Isocyanate-functionalized carrageenans as absorbents for the removal of Carbamazepine and Diclofenac from aqueous solutions

S. G. Nanaki[1], G. Z. Kyzas[1,2], M. Papageorgiou[3], C. Kouloktsi[1], D. N. Bikiaris[1*], D. A. Lambropoulou[3]

[1]Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece.
[2]Laboratory of General and Inorganic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR–541 24 Thessaloniki, Greece.
[3]Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR–541 24 Thessaloniki, Greece.
*Corresponding author: Email: dbic@chem.auth.gr

Abstract

Drugs are of scientific and public concern not only for their benefits but also as newly recognized classes of environmental pollutants. Many of these drug compounds are not completely removed by wastewater treatment plants (WWTPs). Recently, the removal of drugs by adsorption is characterized as one of the most promising techniques, due to its convenience once applied into current water treatment processes. Carrageenans are hydrophilic polymers that hydrate, swell and/or dissolve in aqueous environment. These properties make them suitable as biosorbents. In this study iota- and kappa- carrageenans were functionalized with isocyanate groups and used as super-adsorbent materials for the removal of Carbamazepine and Diclofenac from aqueous solutions. Adsorption and desorption studies followed by kinetic modelling were conducted, while TGA, XRD and FT-IR were used to characterize carrageenans before and after adsorption.

Keywords: carbamazepine; diclofenac; carrageenans; adsorption; kinetic modelling

1. INTRODUCTION

Drugs are among the most hazardous environmental classes of pollutants due to their toxicological properties and their utilization is expected to be increased due to a growing and aging population and an augmented reliance on drug treatment. Many of these compounds are not completely eliminated after their consumption by humans or animals and posteriorly excreted as slightly transformed product or even unchanged to wastewater treatment plants (WWTPs) [1]. Carbamazepine and diclofenac draw attention being the most frequently detected pharmaceutical residues in water bodies so far. Carbamazepine (CBZ) is an anticonvulsant and analgesic drug that is used to treat seizures and nerve pain such as trigeminal neuralgia and diabetic neuropathy. It is also used to treat bipolar disorder. Its low affinity for organic substrate renders it difficult to remove from wastewaters. Diclofenac is a nonsteroidal anti-inflammatory drug taken or applied to reduce inflammation and as an analgesic reducing pain in certain conditions that is found in high concentrations in water waste.

Carrageenans are hydrophilic polymers that have the ability to hydrate, swell and/or dissolve in aqueous environment. They are composed of D-galactose residues linked alternately in 3-linked-β-D-galactopyranose and 4-linked-α-D-galactopyranose units and they are classified according to the degree of the substitution that occurs on their free hydroxyl groups. Due to their properties, carrageenans have already been used as adsorbent materials for removal of metals and organic

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pollutants [2-3]. In this study iota- and kappa- carrageenans were modified with tolulene di-isocyanate and used as adsorbent for two drugs; carbamazepine and diclofenac.
Figures 1 and 2 show the chemical structure of Carbamazepine and Diclofenac respectively.

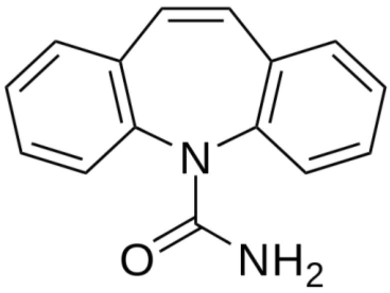


Figure 1. Chemical structure of Carbamazepine

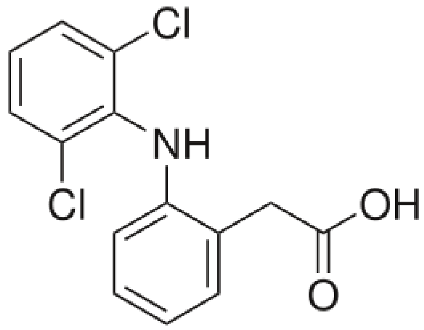


Figure 2. Chemical structure of Diclofenac

2. MATERIALS AND METHODS

2.1. Materials

Iota-carrageenan (Gelcarin GP-379NF) and kappa-carrageenan (Gelcarin GP-812NF) were kindly supplied by FMCBioPolymer (Netherlands). Tolylene-2,4-diisocyante (assay 95%) was purchased from Sigma-Aldrich. Carbamazepine (purum ≥ 99.0%) was purchased from Acros Organics. Diclofenac sodium (purum ≥ 98.5%) was purcused from Sigma-Aldrich. All other solvents used were of analytical grade and those used for HPLC analysis were of HPLC grade.

2.2. Preparation of isocyanate-functionalized carrageenans

Iota- or kappa- carrageenan (5g) respectively was inserted in round bottomed flask containing 50mL of dimethylsulfoxide (DMSO) and stirred at room temperature till suspension was formed. Then, 15mL tolylene diisocyanate (TDI) were inserted to the flask and vigorous stirring was performed at 50^{o}C for 4 hours. The formed gel was cut into pieces and soaked in 100 mL dichloromethane (DCM) under magnetic stirring for 2 hours in order to remove DMSO and unreacted TDI. Further purification was done by inserting the material in distilled water at 80^{o}C for 3 hours for the removal of unreacted carrageenan and finally wash was ethanol was conducted and the synthesized material was left to dry under vacuum. The prepared isocyanate-functionalized iota (iCar-TDI) and kappa (kCar-TDI) was further chopped using cutter mill and particle size of about 100 μm was taken and stored in a desiccator till further use.

2.3. Characterization techniques

The spectra were collected using a Perkin-Elmer FT-IR spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany) between 450 and 4000 cm^{-1} at a resolution of 4 cm^{-1} using 20 co-added scans. All spectra submitted to baseline correction and normalization to 1.
XRD patterns were taken using a Rigaku Mini Flex diffractometer with Bragg-Brentano geometry (θ, 2θ) and a Ni-filtered CuKa radiation. The samples were scanned over the internal range of 5-60°, step 0.02^{o}, speed 2.0 ^{o}/min.

TGA analysis was carried out with a SETARAM SETSYS TG-DTA 16/18. Samples (6.0 ± 0.2 mg) were placed in alumina crucibles and heated from ambient temperature to 800 °C in a 50 mL/min flow of N_2 at heating rates of 20 °C/min.

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2.4. HPLC analysis

Quantitative analysis of Carbamazepine and Diclofenac was performed using a Shimadzu HPLC prominence system (Kyoto, Japan) consisting of a degasser (DGU-20A5), a liquid chromatograph (LC-20 AD), an auto sampler (SIL-20AC), a UV/Vis detector (SPD-20A) and a column oven (CTO-20AC). The column used was a C18 (120 Å, 250 mm x 4.6 mm, 5 μm, CNW Athena).

For Carbamazepine the temperature was set at 40 °C. Water (H_2O), acetonitrile (ACN) and methanol (MeOH) were the elution solvents. The samples were eluted by isocratic flow H_2O/ACN/MeOH 30/10/60 v/v/v and the flow rate was 1mL/min. The total run time was 8 min and the retention time was 4.96 min. The injection volume was 10 μL. Chromatographic data were acquired at the wavelength of 235 nm.

For Diclofenac the temperature was set at 20 °C. Water (H_2O) containing 0.12% v/v acetic acid and methanol (MeOH) were the elution solvents. The samples were eluted by isocratic flow H_2O/MeOH 20/80 v/v and the flow rate was 1mL/min. The total run time was 12 min and the retention time was 7.52 min. The injection volume was 20 μL. Chromatographic data were acquired at the wavelength of 279 nm.

2.5. Adsorption experimental procedure

2.5.1. Carbamazepine

Batch experiments (all experiments were run in triplicate) were carried out using 1 g/L of adsorbent each time (m = 0.03 g of adsorbent's mass were added to V = 30 mL of deionized water in a conical flask). Samples were taken at predetermined time intervals and filtered using 45 μm pore size filtration membrane (Whatman, purchased by Sigma-Aldrich). For the pH-effect experiments (C_0 = 30 mg/L), the solution pH was initially adjusted with aqueous solutions of acid or base (0.01 mol/L of HCl and/or 0.01 mol/L NaOH) to reach pH values of 2-12. The agitation rate was fixed at N = 150 rpm for all adsorption-desorption tests using shaking incubator (Julabo SW-21C, Seelbach, Germany) under a controlled temperature. Isotherms were taken running the adsorption experiments with various initial metro concentrations (C_0 = 0-100 mg/L) at three different temperatures (T = 25, 45, 65 °C) for 24 h (contact time). Kinetic tests were performed using C_0 = 15 mg/L at 25 °C (at pH = 2 and 10) for different contact-time intervals during adsorption (t = 0-4 hrs).

2.5.2. Diclofenac

Batch experiments (all experiments were run in triplicate) were carried out using 0.5 g/L of adsorbent each time (m = 0.015 g of adsorbent's mass were added to V = 30 mL of deionized water in a conical flask). Samples were taken at predetermined time intervals and filtered using 45 μm pore size filtration membrane (Whatman, purchased by Sigma-Aldrich). For the pH-effect experiments (C_0 = 30 mg/L), the solution pH was initially adjusted with aqueous solutions of acid or base (0.01 mol/L of HCl and/or 0.01 mol/L NaOH) to reach pH values of 2-12. The agitation rate was fixed at N = 150 rpm for all adsorption-desorption tests using shaking incubator (Julabo SW-21C, Seelbach, Germany) under a controlled temperature. Isotherms were taken running the adsorption experiments with various initial metro concentrations (C_0 = 0-100 mg/L) at three different temperatures (T = 25, 45, 65 °C) for 24 h (contact time). Kinetic tests were performed using C_0 = 30 mg/L at 25 °C (at pH = 6). PH=6 was selected as it was found to be the optimum value according to pH-effect tests for different contact-time intervals during adsorption (t = 0-4 hrs).

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3. RESULTS AND DISCUSSION

3.1. Characterization of adsorbents

Figure 3 shows FT-IR spectra of net and functionalized with TDI carrageenans. As can be seen there were present all the characteristic peaks of net carrageenans; a broad peak at 3600 – 3200 cm^{-1} owning to O–H interactions, 1645-1655 cm^{-1} (carbonyl group stretching), 1267cm^{-1} (O=S=O asymmetric stretching), 1156 cm-1 (C–O–C asymmetric stretching), 1067-1074cm^{-1} (S–O symmetric stretching), 1027-1038 cm^{-1} (C–O stretching), 928-935 cm^{-1} (C–O–C stretching in 3,6-anhydrogalactose) and 852 cm^{-1} (C–O–S) stretching in a (1-3)-D-galactose.

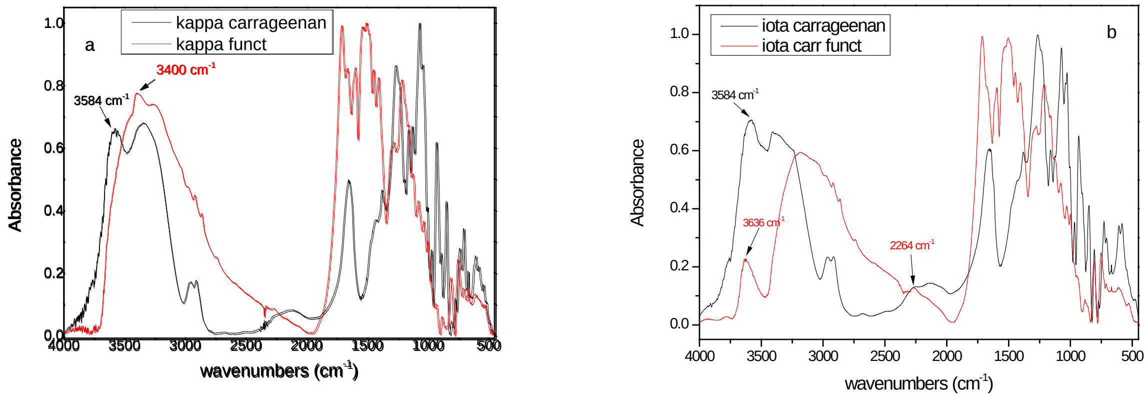


Figure 3. FTIR spectra of a) kappa- and kappa-functionalized carrageenans and b) iota- and iota-functionalized carrageenans.

As observed in kappa-modified FT-IR spectra a new was formed at 3400 cm^{-1} owning to N-H stretching vibrations. In advance, there are present two new peaks at 1662 and 1710 cm^{-1} owning to C=O stretching vibration and a peak at 1542 cm^{-1} owning to N-H stretching of urethane linkage. In addition, the absence of peak at 2275cm^{-1} owning to N=C=O group, confirmed the absence of unreacted TDI. Analogous are the observation for iota-modified carrageenan.

XRD was used to examine if there was any change to the physical state of carrageenans (Figure 4). As it was referred in previous study carrageenans shows a wide broad peak indicating their amorphous state. The addition of –NCO groups didn't show to affect the amorphous state and the resulting cross-linked carrageenans showed also a wide broad peak.

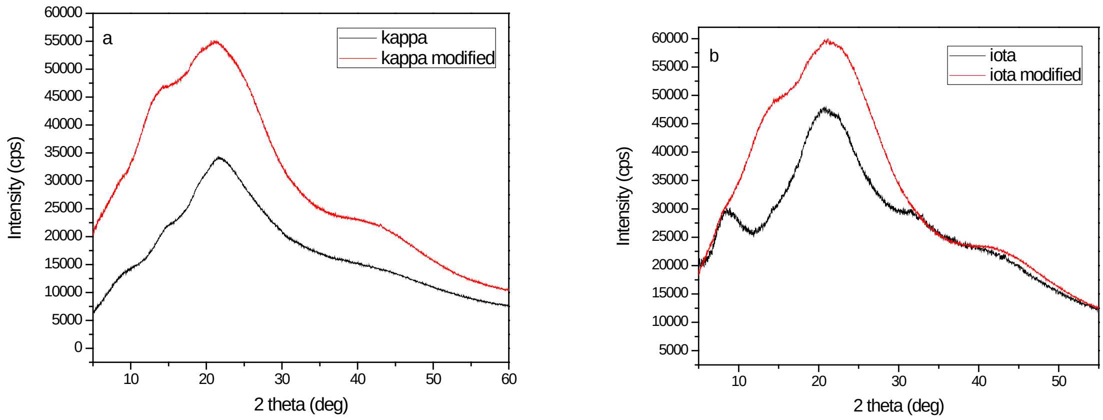


Figure 4. XRD patterns of a) kappa and modified with TDI and b) iota and modified with TDI carrageenans

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In order to assess the thermal stability of the cross-linked carrageenans, thermal gravimetric analysis (TGA) was carried out. Figure 5 shows TGA curves of kappa- and iota- carrageenanan and kappa- and iota- -NCO functionalized carrageenans. As can be seen, thermal degradation profile of –NCO functionalized carageenans turned to be quite different compared to that of neat carrageenans. Carrageenans cross-linked with TDI showed reduced thermal degradation stability due to -NCO groups. In advance kappa-carrageenan showed to be more resistant to thermal stability than iota-carrageenan.

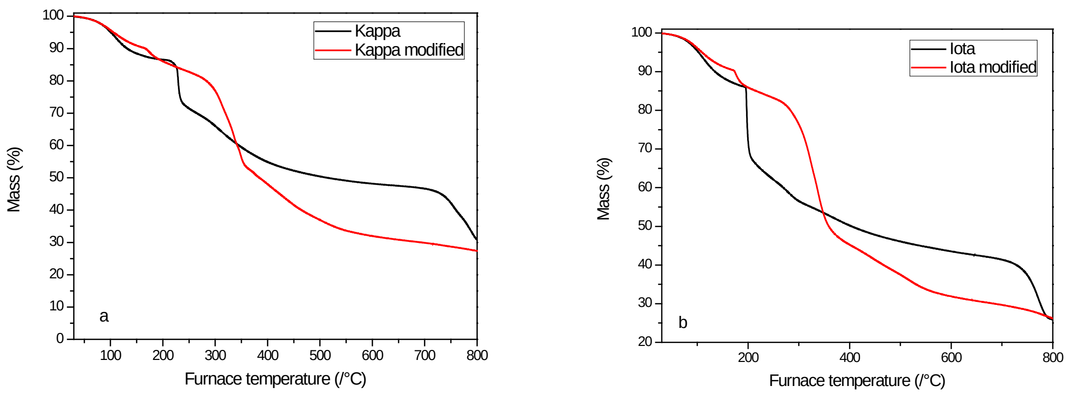


Figure 5. TGA curves of a) kappa and kappa-TDI carrageenans and b) iota and iota-TDI carrageenans.

3.2 Adsorption and desorption studies

3.2.1. Carbamazepine

Figure 6 shows the removal of carbamazepine from various pH values. It was found that the best removal was succeeded at strongly acidic and strongly basic values (pH 2 and 12 respectively). PH=2 and pH=10 were selected for further study according to pKa values of carbamazepine (pKa=2.3 and 13.9).

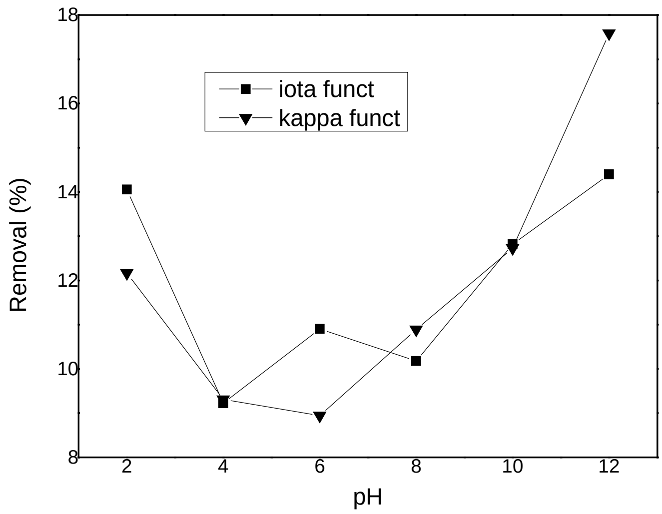


Figure 6. Influence of the solution pH on adsorption

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Figure 7 shows the influence of contact time during adsorption. As can be seen at pH value 2, for both materials and till 150 min, carbamazepine adsorbed gradually and after that time no further adsorption was observed. For pH value 10, the corresponding time was 120 min, i.e. a decrease of 30 minute was observed.

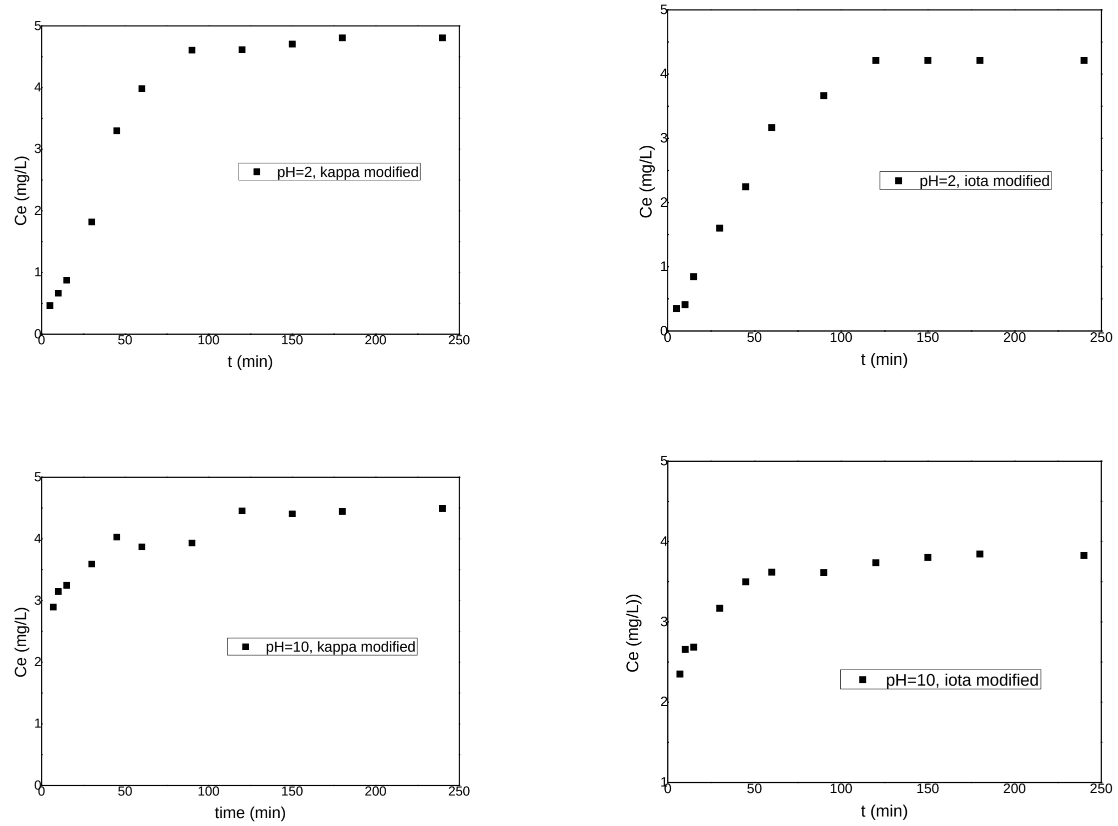


Figure 7. Influence of contact time during adsorption

Desorption studies at different pH values was also conducted and the results are shown in Table 1. As can be seen at pH=8 was succeeded the higher percentage desorption of carbamazepine.

Table 1. Desorption study at different pH values

Sample	Kappa modified	Iota modified
	Desorption (%)	Desorption (%)
pH = 2	22.32	19.01
pH = 4	22.58	35.60
pH = 6	26.76	29.47
pH = 8	30.45	42.05
pH = 10	28.83	31.62
pH = 12	23.25	37.77

3.2.2. Diclofenac

Figure 8 shows the influence of pH during adsorption of diclofenac. As can be seen, the best removal was succeeded at pH value 2. However, at pH values 2 and 4 it was found a divergence between the theoretically and HPLC determined concentration, may because hydrolysis or degradation occurs. For that reason pH 2 and 4 was rejected and pH 6 was selected for further adsorption studies.

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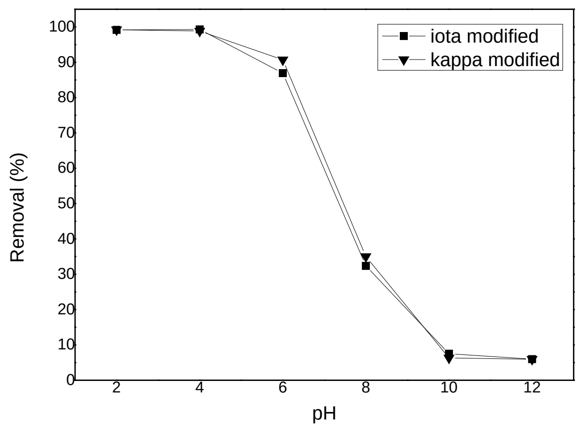


Figure 8. Influence of pH during adsorption study

The influence of contact time during adsorption is shown in Figure 9.

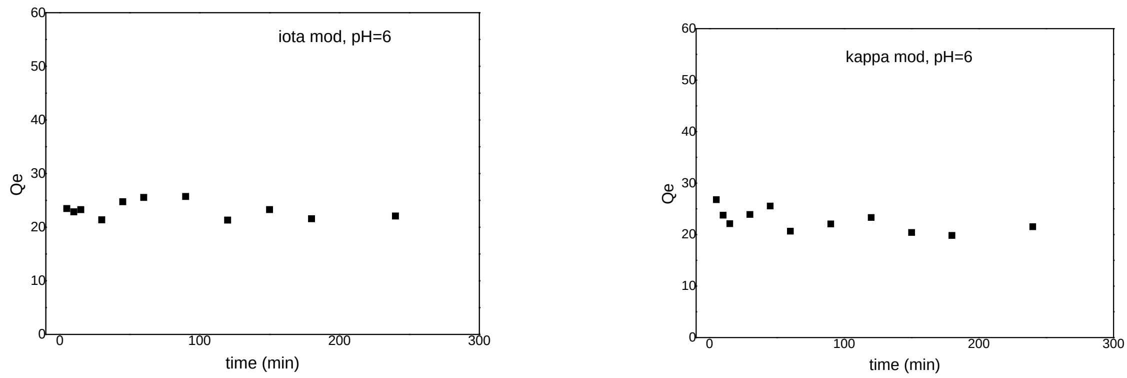


Figure 9. Influence of contact time

Finally, Table 2 shows the results of adsorption study. It was found that maximum desorption of diclofenac was achieved at pH 8.

Table 2. Desorption study at different pH values

Sample	Kappa modified	Iota modified
	Desorption (%)	Desorption (%)
pH = 2	5.07	4.79
pH = 4	7.43	5.87
pH = 6	11.14	9.00
pH = 8	23.39	13.67
pH = 10	9.82	9.73
pH = 12	12.91	10.57

Conclusions

Iota and kappa carrageenan were successfully functionalized with isocyanate groups and found to be stable till 155^{o}C. The above materials were used for the removal of carbamazepine and diclofenac from water. As optimum pH value for the removal of carbamazepine was found to be 2 and 10 while for diclofenac was 6. Carbamazepine showed that the removal was succeeded in the first 150 minutes at pH 2 for both iota- and kappa- functionalized carrageenans, while for pH 10 the

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time showed a decrease of 30 minutes, i.e. the removal was practically completed at 120 minutes. Diclofenac showed that reached its high adsorption at the first 60 minutes. Desorption studies showed that carbamazepine was successfully desorbed from both materials, showing its maximum desorption at pH 8. The percentage desorption showed a high difference between kappa- and iota-functionalized carrageenans, with the second one to have a value of 12 units higher (30% for kappa- and 42% for iota). Analogous is the observation for diclofenac, which showed its higher percentage desorption at pH 8. Diclofenac showed that was able to be easier desorbed from kappa-functionalized carrageenan than from iota-carrageenan. The difference reached 10 units (23.5% for kappa and 13.5% for iota).

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References
[1] Lambropoulou D., Nollet L., 2014. *Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects*. 1st Ed, John Wiley and Sons Ltd.

[2] G.R. Mahdavinia, R. Zhalebaghy, 2012. Removal kinetic of cationic dye using poly (sodium acrylate)-carrageenan/na-montmorillonite nanocomposite superabsorbents, *Journal of Materials and Environmental Science*, **3**, 895-906.

[3] Nanaki, S.G., Kyzas, G.Z., Tzereme, A., Papageorgiou, M., Kostoglou, M., Bikiaris, D.N., Lambropoulou, D.A. 2015. Synthesis and characterization of modified carrageenan microparticles for the removal of pharmaceuticals from aqueous solutions. *Colloids and Surfaces B: Biointerfaces,* **127,** 256-265.

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Removal of pharmaceuticals by novel crosslinked copolymer adsorbents based on acrylic acid and vinyl imidazole

A. Koltsakidou[1], Z. Terzopoulou[2], K. V. Adam[2], D. N. Bikiaris[2], D. A. Lambropoulou[1*]

[1] Laboratory of Environmental Pollution Control, Department of Chemistry,
Aristotle University of Thessaloniki, Greece.
[2] Laboratory of Polymer Chemistry and Technology, Department of Chemistry,
Aristotle University of Thessaloniki, Greece.
* Corresponding author: Email: dlambro@chem.auth.gr

Abstract

Novel random copolymers based on acrylic acid (AA), vinyl imidazole (VI) and crosslinked trimethylopropane trimethacrylate (TRIM) were synthesized and used for the adsorption and removal of 3 drugs commonly found in wastewaters. Adsorbent materials were characterized by FTIR and TGA, and the effect of pH and comonomer composition on the adsorption ability was studied. The chosen drugs were atenolol (ATE), diclofenac (DIC) and ibuprofen (IBU). Each drug was found to adsorb more effectively on different copolymer compositions, as well as in different pH conditions, due to their varying drastic groups and therefore different interactions with polymers of varying comonomer contents.

Keywords: pharmaceuticals; adsorption; wastewater; polymers; toxicity.

1. INTRODUCTION

The occurrence of pharmaceuticals and their transformation products (TPs) has been documented worldwide in various compartments of the water cycle including both natural and technical aquatic systems impacted by wastewater discharges and waste disposal sites [1]. Consequently, there is a growing awareness of the risks related to the emission of pharmaceuticals and their TPs in the aquatic environment [2]. To reduce the potential risk caused by these compounds in treated wastewater discharged to aquatic environments, their removal in water treatment plants is considered as an important technological challenge [3]. Adsorption is one of the most promising techniques used to remove pharmaceuticals from water [4]. Diclofenac, ibuprofen and atenolol, are three of the most frequently detected pharmaceuticals present in wastewater. The first two are anti-inflammatory drugs used worldwide, while the last one is used as a beta-blocker. Polyacrylic acid (PA) is a hydrophilic polymer widely used as an adsorbent for metal ions, dyes and drugs. In a water solution at neutral pH, PA is an anionic polymer, i.e. many of the side chains of PA will lose its protons and acquire a negative charge. This makes PA a polyelectrolyte, with the ability to absorb and retain water and swell to many times their original volume [5]. Poly(1-vinyl imidazole) (PVI) is a basic polymer that contains two active centers. Due to its basic character, in can be protonated in certain pH conditions, and therefore successfully adsorb pollutants with opposite charge [6]. Both polymers are water-soluble and for this reason the addition of a cross-linker is required for use in adsorption of compounds from aquatic media. TRIM was chosen because it is a trifunctional monomer that can generate a complex network of macromolecular chains that will contain the drastic groups of AA and VI that can enhance adsorption. The aim of this study was to use copolymers with different AA/VI ratio and to evaluate their effectiveness to the chosen drug contaminates removal.

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2. MATERIALS AND METHODS

2.1. Materials

All reagents, such as AA, VI and TRIM as well as pharmaceutical compounds (ATE, DIC and IBU) were supplied by Sigma Aldrich. All solvents used were of analytical grade and also supplied by Sigma-Aldrich.

2.2. Synthesis of polymers

The adsorbents used were synthesized using different AA/VI ratios by bulk polymerization and TRIM as the cross-linking agent. Briefly, AA and/or VI monomers were dissolved in ACN:$CHCl_3$ (19:1, v/v). Then, cross-linking reagent (TRIM), and radical initiator (AIBN) dissolved also in ACN:$CHCl_3$ (19:1, v/v) were added to the reaction mixture. The solution was purged with nitrogen for 15 min and sealed. The mixture was subsequently polymerized in an oil bath under stirring, at 60 °C for 2 h. The resulting polymers were washed with $CHCl_3$, filtered and dried under vacuum. The final 5 polymers that were synthesized according to the described procedure and their composition, are presented in Table 1.

Table 1: Materials prepared and their composition

Material	AA (mmol)	VI (mmol)	TRIM (mmol)	ACN:$CHCl_3$ 19:1 (mL)
PA	16	0	16	40
P(VI-PA) 25/75	12	4	16	40
P(VI-PA) 50/50	8	8	16	40
P(VI-PA) 75/25	4	12	16	40
PVI	0	16	16	40

2.3 Characterization techniques

Fourier Transform Infrared spectra of the prepared copolymers (FTIR) were recorded with a Perkin-Elmer FT-IR spectrometer (model FTIR-2000, Perkin Elmer, Dresden, Germany). Infrared (IR) absorbance spectra were obtained between 450 and 4000 cm^{-1} at a resolution of 4 cm^{-1} using 20 co-added scans. Thermogravimetric analysis was carried out with a Setaram Setsys TG-DTA 16/18. Samples of 4.0 ± 0.2 mg were placed in alumina crucibles. An empty alumina crucible was used as reference. All materials were heated from ambient temperature to 600 °C in a 50 ml min^{-1} flow of Nitrogen at heating rate of 20 °C min^{-1}. Continuous recordings of sample temperature, weight, and heat flow were performed.

2.4 Adsorption – desorption experimental design

Batch experiments were carried out using 1 g/L of adsorbent (m = 0.01 g of adsorbent's mass were added to V = 10 mL of water in a conical flask). The influence of pH over the adsorption process was studied by mixing the sorbent with drug solution (10 mg/L). Immediately after mixing, the suspension was allowed to bind dyes by shaking for 24h. The temperature was maintained constant at 25±1°C using water bath (Grant). The pH value, 4, 6 and 10, was kept constant throughout the adsorption process. Methanol was used as a desorption solvent.

2.5 LC-DAD-ESI/MS analysis

The LC-MS system consisted of a SIL 20A auto sampler with the volume injection set to 20μL and LC-20AB pump both from Shimadzu (Kyoto, Japan). The separation of the analytes was contacted by a C18 (Restek) analytical column 150 4.6 mm with 5μm particle size (Restek, USA). The

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samples were analyzed using the ESI interface in positive and negative ionization mode. For the analysis, a gradient elution was performed by a binary gradient composed of solvent A (water with 0.1% formic acid) and solvent B (methanol with 0.1% formic acid).

3. RESULTS

3.1 FTIR spectroscopy

The prepared copolymers were first characterized by FTIR spectroscopy and the recorded spectra are presented in Figure 1. Furthermore, the characteristic peaks correspond to the functional groups of each one different monomer, as shown in Table 2. The presence of hydroxyls, carboxyls, carbonyls and the imidazole ring of PVI is confirmed, indicating the successful synthesis of the copolymers.

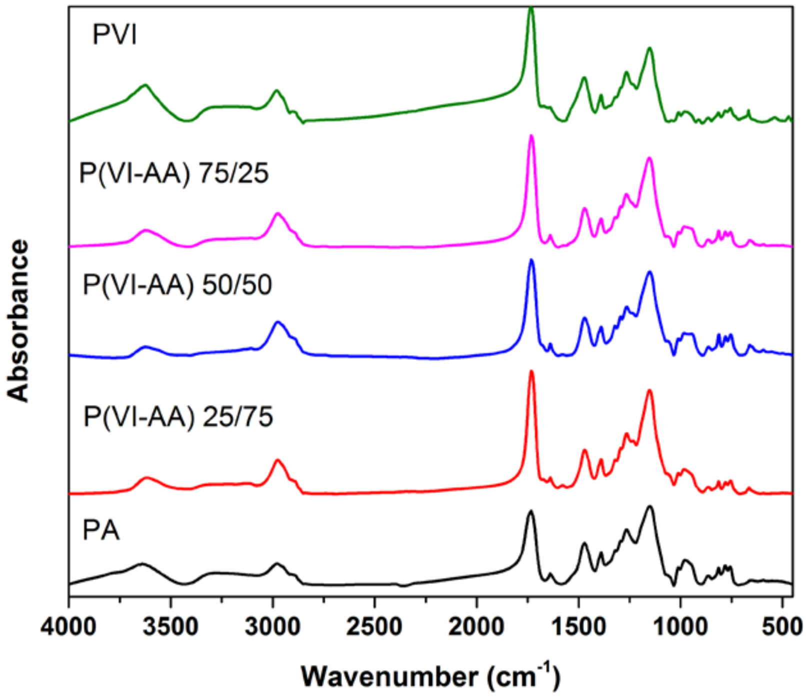


Figure 1: FTIR spectra of the prepared polymers

Table 2. FTIR spectra peaks

Wavenumber (cm^{-1})	Assignment
3620	-OH
2980	C-H
1740	C=O
1467	C=C or C=N
1260	Ester C-O
1150	Carboxylic C-O
960	Imidazole C-H
670	Imidazole C-H

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3.2 TGA analysis

Thermogravimetric analysis was used to study the thermal stability of the materials. Mass loss curves are presented in Figure 2.

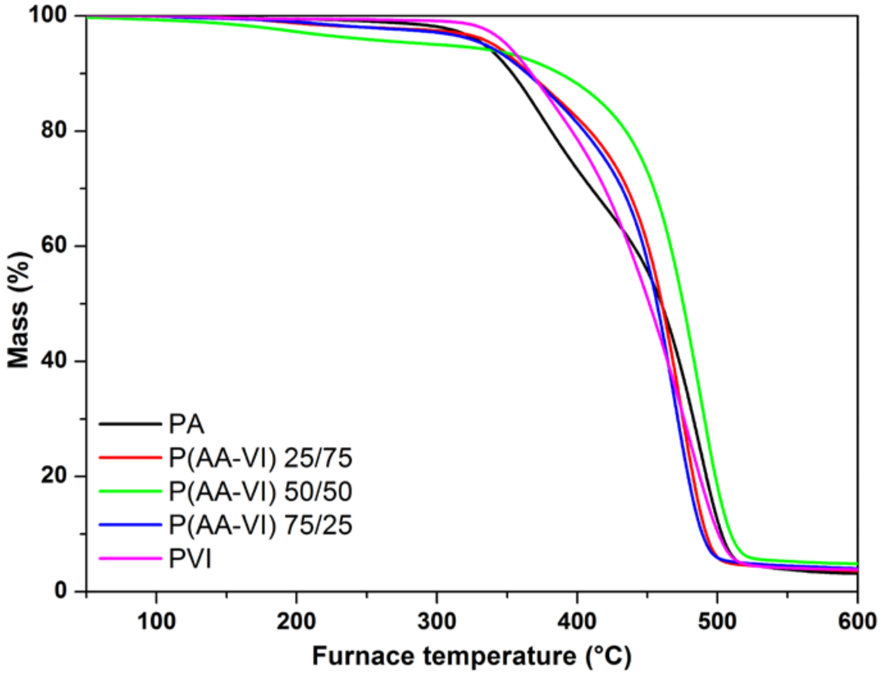


Figure 2: Mass loss curves oft he materials

The temperature at which degradation begins (T_i) and the temperature at which the degradation takes place in the highest rate (T_p), and are presented in Table 3. All 5 materials exhibit excellent thermal stability, since the degradation starts at 330 ° C and above. Introduction of the bulky imidazole ring in the polymer chain enhances the thermal stability of materials with optimum monomer ratio 50/50.

Table 3. Characteristic thermal degradation temperatures of the polymeric materials.

Material	T_i (°C)	T_p (°C)
PA	330	487
P(AA-VI) 25/75	336	474
P(AA-VI) 50/50	435	487
P(AA-VI) 75/25	340	470
PVI	385	487

Up to 100 °C water is released in all 5 polymers. All materials degrade at two stages. The first degradation stage of PA at 300-370° C is probably due to polyacrylic acid, while the first degradation stage in PVI is of vinylimidazole, at temperature 320-390 °C. The second degradation stage begins after 400 °C, due to crosslinking, and is completed at 530 °C. The highly improved thermal stability of P (AA-VI) 50/50 can be caused by extensive networking and intramolecular and intermolecular bonds between the PA and PVI chains.

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3.3. Effect of pH on adsorption

According to adsorption experiments, atenolol which carries hydroxyl and amino groups, was absorbed only by the material with 100% AA content. Adsorption varied from 20 to 60% with a maximum at pH 10. The effect of pH and copolymer composition on the adsorption of atenolol is presented in Figure 3.

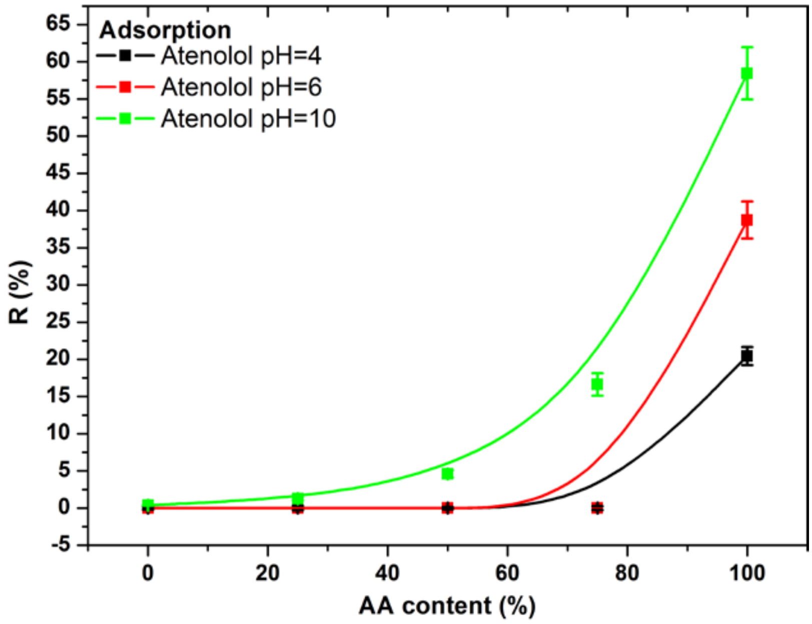


Figure 3: Effect of pH and copolymer composition on the adsorption of atenolol.

Diclofenac having reactive groups hydroxyl, amino and chloride molecules presented adsorption onto all materials with a maximum absorption at pH 4, for the material containing 100% AA (PA). Diclofenac's adsorption was very high (73-100%) for all materials. The effect of pH and copolymer composition on the adsorption of diclofenac is presented in Figure 4.

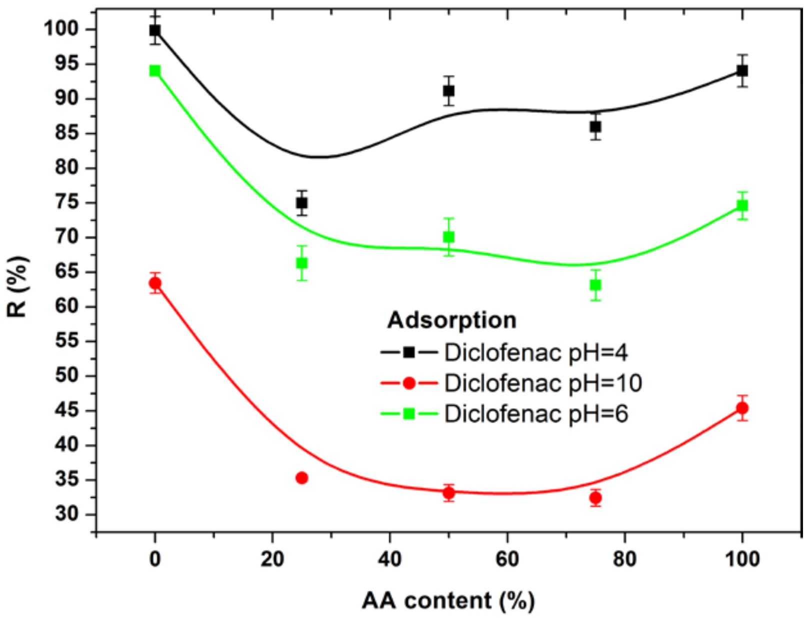


Figure 4: Effect of pH and copolymer composition on the adsorption of diclofenac.

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Ibuprofen presented 95% adsorbance for pH 4 on PA. Desorption was notable mainly for copolymers with 25, 50 and 75% AA content. The effect of pH and copolymer composition on the adsorption of ibuprofen is presented in Figure 5.

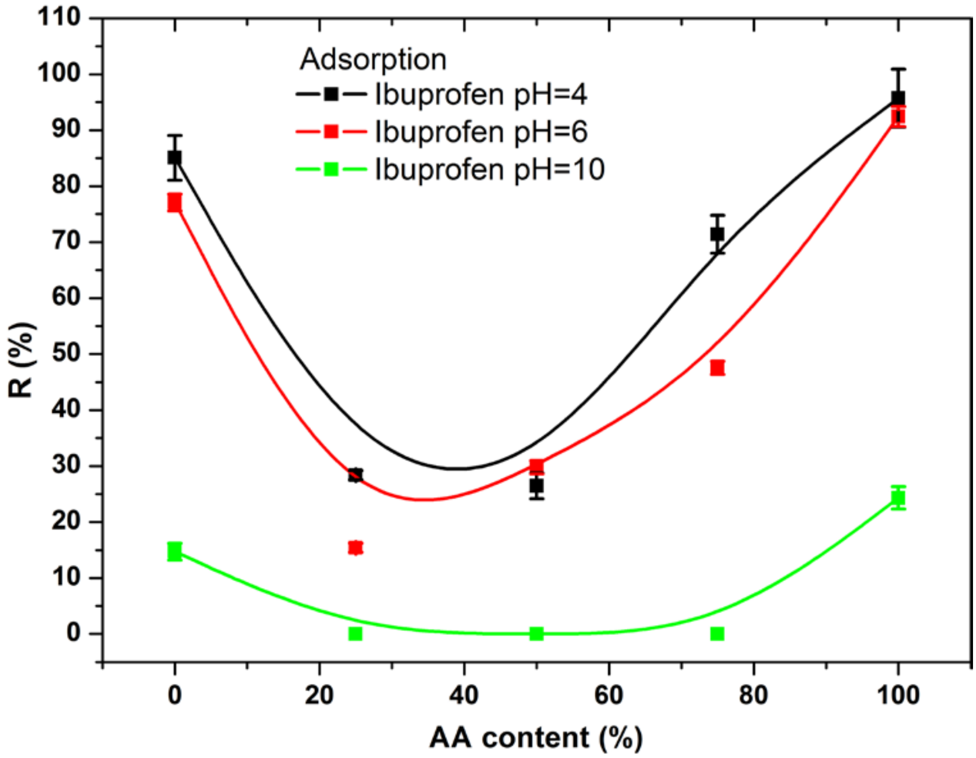


Figure 5: Effect of pH and copolymer composition on the adsorption of ibuprofen.

A shifting of the peak was observed at PA's spectrum after adsorption of atenolol due to hydroxyl groups, indicating the establishment of hydrogen bonds between the adsorbent and the drug. Similarly, the spectrum of PA after adsorption of diclofenac presents shifting at the hydroxyl peak. The absence of shifts of the peaks of PVI indicate that the absorption is probably due to electrostatic interactions.

4. CONCLUSIONS

Highly crosslinked and thermally stable polymeric adsorbents were successfully prepared with bulk polymerization. The homopolymers PA and PVI and their random copolymers successfully adsorbed 3 different drugs from aquatic media, with different optimum comonomer compositions as also different optimum pH conditions that depended on the molecular structure of each drug. Adsorption was found to occur both chemically, with hydrogen bonding proved by FTIR spectra, and physically or ionically, since both PA and PVI can act as polyelectrolytes that can bond ionically with ionized groups of the drugs.

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References

[1] Lambropoulou D., Nollet L., 2014. *Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects*. 1st Ed, John Wiley and Sons Ltd.

[2] Kyzas G., Koltsakidou A., Nanaki S., Bikiaris D., Lambropoulou D., 2015. Removal of beta-blockers from aqueous media by adsorption onto graphene oxide. *Science of The Total Environment*, **537,** 411-420.

[3] Vidal C.B., dos Santos A.B., do Nascimento R.F., Bandosz T.J., 2015. Reactive adsorption of pharmaceuticals on tin oxide pillared montmorillonite: Effect of visible light exposure. *Chemical Engineering Journal*, **259**, 865-875.

[4] Fukahori S., Fujiwara T., Ito R., Funamizu N**.,** 2011. pH-Dependent adsorption of sulfa drugs on high silica zeolite: Modeling and kinetic study. *Desalination*, **275 (1-3),** 237-242.

[5] da Fonseca R.J., Segatelli M.G., Borges K.B., Tarley C.R.T., 2015. Synthesis and evaluation of different adsorbents based on poly(methacrylic acid–trimethylolpropane trimethacrylate) and poly(vinylimidazole–trimethylolpropane trimethacrylate) for the adsorption of tebuthiuron from aqueous medium . *Reactive and Functional Polymers,* **93,** 1-9.

[6] Molina M.J., Gómez-Antón M.R., Piérola I.F., 2004. Factors driving the protonation of poly(N-vinylimidazole) hydrogels . *Polym. Sci. B Polym. Phys.,* **42 (12),** 2294-2307.

Nitrate and phosphate uptake by immobilized *Chlamydomonas reinhardtii* cells

J. Papantoniou, A. Papadopoulou, A. Polydera, D. Gournis, P. Katapodis*, H. Stamatis

Laboratory of Biotechnology, Department of Biological Applications & Technologies,
School of Health Sciences, University of Ioannina, 45110 Greece.
*Corresponding author: Email: pkatapo@cc.uoi.gr

Abstract

The effect of co-immobilization of Chlamydomonas reinhardtii cells with graphene, graphene oxide, and graphene anthracene in calcium alginate on nitrate and phosphate uptake rate was studied and compared with nitrate and phosphate consumption of solely immobilized cells. The optimum conditions of alginate concentration, cell loading, bead diameter and light intensity for nitrate and phosphate uptake rates were investigated. Immobilized cells accomplished a 100% nitrate and 90% phosphate removal. Furthermore, removal of phosphate and nitrate by immobilizes cells of microalgae C. reinhardtii were made in semi-continuous feed systems. The effectiveness of the process is maintained for more than five re-use cycles.

Keywords: Chlamydomonas reinhardtii; nitrate; phosphate; immobilization; nanomaterials; alginate

1. INTRODUCTION

Large-scale production of wastewater containing nutrients like nitrate and phosphates have been identified as the main cause of eutrophication in natural waters. Eutrophication has become a major problem in water quality management. Secondary treatments of domestic and agro-industrial wastewater still release large amounts of phosphorus and nitrogen [1]. Wastewater treatment using autotrophic microalgae has been proposed as an economical process removing nitrogen and phosphorus at a high efficiency level. However, there are some disadvantages such as costly biomass harvesting and the need for large culturing areas [2].

Immobilization of microalgae in polymeric matrices appears to be one of the best techniques and is cost-effective for separating microalgae from their culture medium in tertiary wastewater treatment with microalgae [3-5]. Moreover, higher nutrient removal efficiencies by immobilized cells in comparison with free microalgae cell have been reported [6-9]. In addition to wastewater treatment, immobilized algae systems have several applications, which include metal removal, stock culture management and, production of useful chemicals [10]. Interaction between immobilized algae and the matrix, may include effects on cellular physiology [11]. The immobilization matrix could be a synthetic polymer (e.g. acrylamide, polyurethane), or a natural polymer (alginate, carrageenan, agar, collagen); but it must fulfill various requirements, such as photo-transparency, non-toxicity, retention of cellular viability, and stability in the culture medium [12]. Alginate is the most frequent polymer used for algal immobilization. Studies have adequately verified cell viability in the alginate matrix [13-16] and the effectiveness of nutrient removal by these immobilized algae [17–21]. Alginate provides a stable and functional matrix for cell immobilization that keeps cells

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viable in terms of biological parameters including photosynthetic activity and chlorophyll (Chl) content [16, 22].

Nanoparticles (NPs) have attracted enormous attention due to their unique electronic, optical and magnetic properties. They are considered strategic materials for applications in the medical, electronic and food areas, among others [23]. The recently discovered carbon nanomaterial, graphene, is composed of sp2 hybridized carbon atoms arranged hexagonally in a two dimensional structure, resulting in a large surface area on both sides of the planar structure [24]. Due to their unique chemical and physical properties, graphene and its derivatives have found important places in their respective application fields [25-27]. Ggraphene-based nanomaterials increase the operational stability of biomacromolecules including enzymes [28].

In the present work, we examine the effect of alginate co-immobilization of *Chlamydomonas reinhardtii* cells with graphene based nanomaterials on nitrate and phosphate uptake. The optimum conditions of alginate concentration, cell loading, bead diameter and light intensity for nitrate and phosphate uptake rates were investigated.

2. MATERIALS AND METHODS

2.1. Microorganism and culture conditions

An axenic *Chlamydomonas reinhardtii* strain CCAP 11/32C (Culture Collection of Algae and Protozoa) was used for the experiments. The strain was stored in solid Tris–Acetate–Phosphate (TAP) medium [29]. The cells were cultivated photoautotrophicaly in 3N-BBM medium in 250 ml Erlenmeyer flasks at 25 C under continuous illumination with white fluorescence lamps at 80 μE m^{-2} s^{-1}, until they reached the mid-exponential phase of growth.

2.2. Entrapment of microalgae *C. reinhardtii* cells in Ca-alginate beads

The cells were harvested by centrifugation at 5000×g for 5 min, washed twice with TB (Tricine–NaOH buffered, 20 mM, pH 8), and resuspended in alginate solution (1-3 %, w/v). Graphene based nanomaterials (graphene, graphene oxide and graphene anthracene) was added at a final concentration of 10 μg ml^{-1} in the alginate cell suspension. The alginate solution was prepared by mixing 1 to 3 g alginate sodium salt in 100 ml of BBM medium without nitrate and phosphate. The pH was adjusted to 6.5–7.5 with a 10% (w/v) sodium hydroxide solution. Alginate beads were obtained by dropping the alginate cell mixture, through the lumen of an appropriate needle in order to achieve beads diameter from 1 to 6 mm, into a 0.1 M $CaCl_2$ solution at 4°C. After 30 min the beads were rinsed with fresh culture medium and used.

2.3. Nitrate and phosphate uptake experiments

Batch experiments for nitrate and phosphate uptake rates were carried out at 25°C in 250 mL Erlenmeyer flasks containing 100 ml BBM medium with modified concentrations of 1.5 mM $NaNO_3$ and 0.15 mM KH_2PO_4. Beads containing *C. reinhardtii* cells and nanomaterials were placed into the flask (10%, w/v), and illuminated continuously with light according to the experimental requirements (5 to 120 μE m^{-2} s^{-1} measured at the flask surface).

2.4. Analytical determinations

Chlorophyll α concentration determination according to the method described by Eijckelhoff and Dekker [30]. Suspension of microalgae were centrifuged at 2500 rpm at 4 °C for 10 min and then rinsed with acetone (80%), then centrifuged again and analyzed using the mentioned method.

For nitrate determination the method described by Diatloff and Rengel [31] was used. Phosphate was determined using method 4500-P E (ascorbic acid) as described in Standard Methods for the Examination of Water and Wastewater [32].

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2.5. Statistics

Figures and Tables show means of three independent experiments. Each data point represents the mean of triplicates, and error bars represent S.E. of the mean. All of the control and experimental values were subjected to paired t tests. Significant levels for all analyses were set to $p<0.05$. All statistical calculations were done using OriginPro 8.0.

3. RESULTS AND DISCUSSION

3.1. Effect of graphene based nanometerials on nitrate and phosphate consumption by *C. reinhardtii* cells

The nitrate and phosphate consumption of alginate-entrapped *C. reinhardtii* cells with graphene, graphene oxide and graphene anthracene was studied and compared with alginate-entrapped cells without nanomaterial. The initial cell loading in the gel beads was 1 mg dry cells per g gel (50 μg Chl per g gel) and 10 μg of nanomaterial per g gel. The nitrate and phosphate were consumed continuously from initial concentrations of 1.5 mM and 0.15 mM, respectively. The maximum uptake rates were 890±29 μmole nitrate per g dry cells per day and 88±3 μmole phosphate per mg dry cell per day for solely immobilized cells (Fig. 1). When the cells were immobilized in presence graphene and graphene oxide the nitrate consumption increased significantly reaching a rate of 1000±30 μmole g^{-1} d^{-1} (Fig. 1). Similarly, higher phosphate uptake rates was observed for these nanomaterials, in particularly 108±3 and 110±3 μmole mg^{-1} d^{-1} for graphene and graphene oxide, respectively. Furthermore, alginate beads with graphene based nanomaterial not showing any significant nitrate and phosphate removal. The presence of graphene and graphene oxide at concentration of 10 mg per L in 3N-BBM cause an increase of chlorophyll content of *C. reinhardtii* cells although inhibiting slightly the growth (data not shown). In other studies, microalgal composites with multilayer graphene [26] or graphene oxide sheets [27] also achieved significant nitrate uptake rates, without being toxic for the microalgal cells.

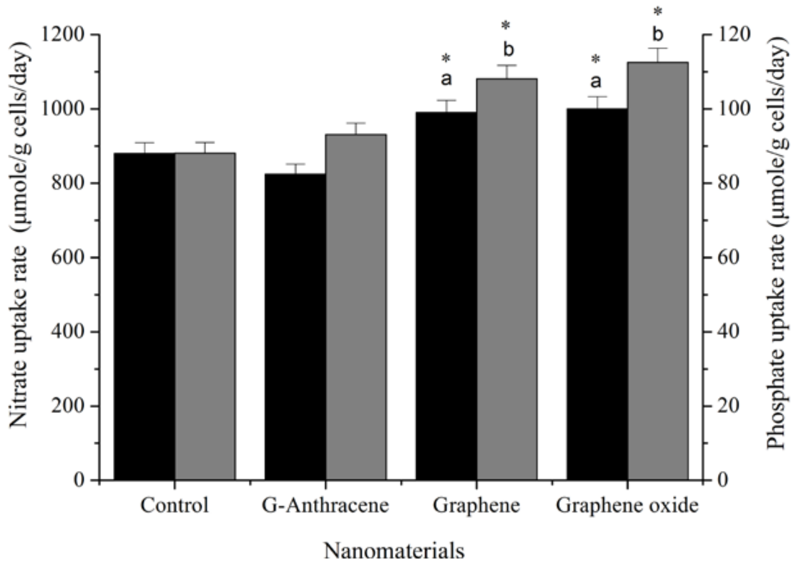


Figure 1. Nitrate (black columns) and phosphate (Grey columns) uptake rates by co-immobilized algal cells of Chlamydomonas reinhardtii with nanomaterials. Control represents immobilized microalgae without nanomaterial. Bars represent ±1 SE. Means within a column for each treatment followed by the same letters do not differ significantly from each other. Means within a column followed by asterisk differ significantly from control.

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3.1.3. Effect of cell loading and alginate concentration on nitrate and phosphate uptake

The concentration of alginate suspension determines the diffusion of substrates through the matrix. The variation of nitrate and phosphate uptake rates according to alginate concentration in the range of 1 to 3 % (w/v) was studied. The initial cell loading in the gel beads was 1 mg dry cells per g gel (50 µg Chl per g gel) and 10 µg of graphene oxide per g gel. An increase in the alginate concentration does not affect significantly the consumption rates of nitrate and phosphate by cells at this range. Similarly, Garbayo et al. showed that a slightly decrease on the consumption rate of nitrate by immobilized *Chlamydomonas einhardtii* cells occurred when the alginate concentration increased from 3 to 6% (w/v) [23]. In order to have better mechanical stability of the beads, 3 % (w/v) alginate in the immobilization procedure has been chosen for the next experiments.

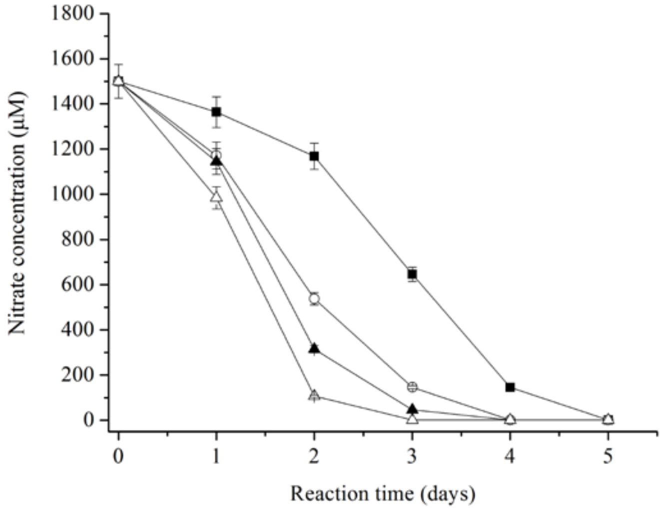


Figure 2. Nitrate uptake from medium as residual concentration by different concentration of immobilized *Chlamydomonas reinhardtii* cells with graphene oxide in alginate beads. Concentration of mg cells per gram of alginate: 1 (■), 2 (○), 4 (▲) and 8(Δ). Bars represent ±1 SE.

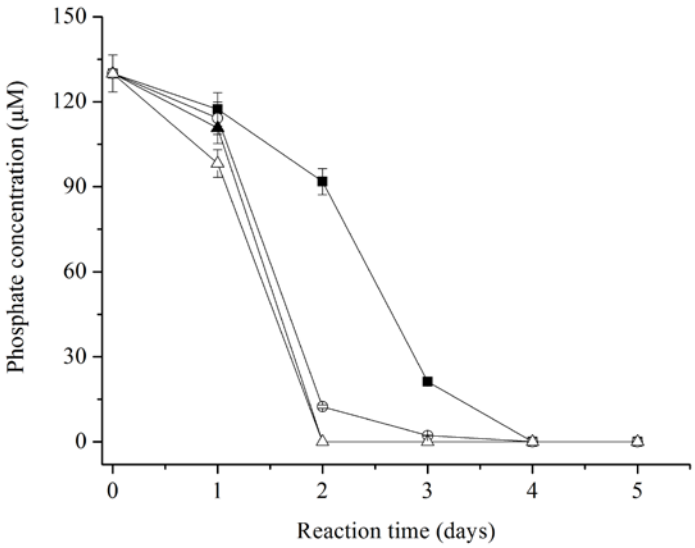


Figure 3. Phosphate uptake from medium as residual concentration by different concentration of immobilized *Chlamydomonas reinhardtii* cells with graphene oxide in alginate beads. Concentration of mg cells per gram of alginate: 1 (■), 2 (○), 4 (▲) and 8(Δ). Bars represent ±1 SE.

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The effect of cell loading (1 to 8 mg dry cells g^{-1} gel and 10 μg of graphene oxide g^{-1} gel) on nitrate and phosphate removal was also studied. As shown in Figure 2 nitrate removal increased as the initial cell loading increased. In particular, nitrate removal was 22%, 64%, 74% and 93% after 2 days for cell loading 1, 2, 4 and 8 mg dry cells per g gel, respectively. Similarly, phosphate removal increased according to initial cell loading, reaching a plateau at 4 mg dry cells per g gel. When the cell loading was 1 mg dry cells per g gel 29% of initial phosphate had been removed after 2 days. Furthermore, the phosphate removal increase to 90% for 2 mg dry cells per g gel and reached 100% for higher cell loading. However, the nitrate and phosphate uptake rates per cell reached maximum values (48 and 5,9 μmole mg^{-1} of cells, respectively) at cell loading 2 mg dry cells per g gel and then decreased as cell concentration in the gel increased. These data suggest a significant influence of shading effect caused by the outermost cells of the beads. A similar profile for nitrate uptake and light-dependent oxygen production by immobilized *Chlamydomonas reinhardtii* cells has been observed previously [12]. High cell loading produces two simultaneous effects that slow down the nitrogen uptake a 'shading' effect produced by the outer cells in the beads over the internal ones, which are not able to sustain the photosynthetic activity and the diffusion of nutrients is difficult because consumed mostly by the outer cells, which also delay consumption of oxygen by the inner cells [33]. The cell loading used for further experiments was 8 mg dry cells per g gel.

3.1.4. Effect of alginate beads diameter on nitrate and phosphate uptake

The effect of alginate beads diameter on nitrate and phosphate removal was investigated. Nitrate and phosphate uptake rates increased with decreasing size of the alginate beads for diameters from 6 to 3 mm, while further diameter reduction did not affect the uptake rates significantly (Figure 5). In particular, the nitrate uptake increased from 540±15 μM nitrate d^{-1} at 6 mm beads diameter to a rate of 815±20 μM d^{-1} at 3 mm beads diameter. Similarly, the phosphate uptake increased from 54±2 μM d^{-1} at 6 mm beads diameter to a rate of 85±2 μM d^{-1} at 3 mm beads diameter. These data suggest that increasing size of beads enhances the substrate diffusion limitations and the shading effect of cells located near the surface of the bead over the internal ones, thus decreasing the nitrate and phosphate uptake rates.

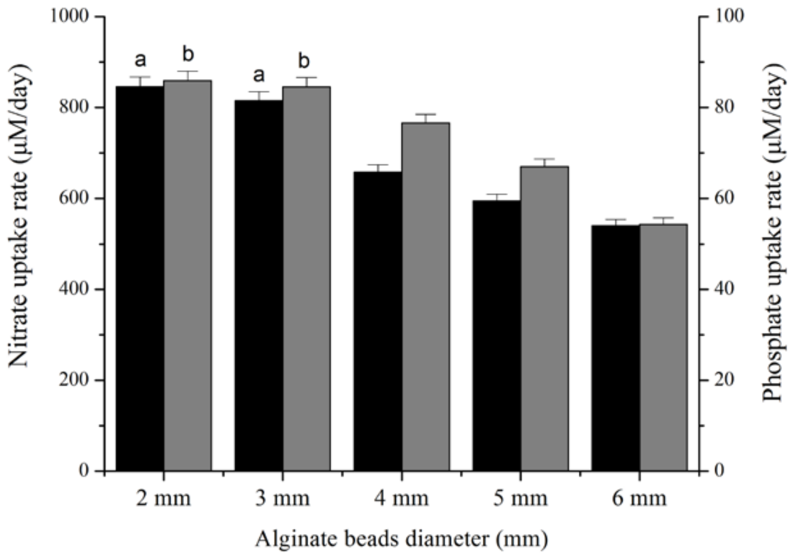


Figure 4. Effect of alginate beads diameter on nitrate and phosphate uptake rate by co-immobilized algal cells of *Chlamydomonas reinhardtii* with graphene oxide. Bars represent ±1 SE. Means within a column for each treatment followed by the same letters do not differ significantly from each other.

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3.1.4. Effect of light intensity and quality of light on nitrate and phosphate uptake

The nitrate and phosphate consumption rate of immobilized cells in presence of graphene oxide was observed under blue and red light at 60 μE m^{-2} s^{-1}. When the cells illuminated with red light the nitrate uptake rate decreased at 30% of the maximum uptake rate determined for white light. Similarly, a decrease in nitrate consumption was observed when the immobilized cells were exposed to blue light illumination (60% of the maximum consumption). The phosphate uptake rate was negligible in both red and blue illuminations. The results is in agreement with previous observations [16]. The effect of light intensity of white light on nitrate and phosphate uptake rates of immobilized cells is illustrated in Figure 4. The nitrate and phosphate uptake rates shows a significant and progressive increment as the light intensity increases from 5 to 120 μE m^{-2} s^{-1}. The maximum nitrate and phosphate consumption rates were observed under 120 μE m^{-2} s^{-1} were 1080±30 and 120±4 μM d^{-1}, respectively. At higher light intensity not a significant consumption increment was observed, indicating light saturation of the active microalgae cells in the specific system.

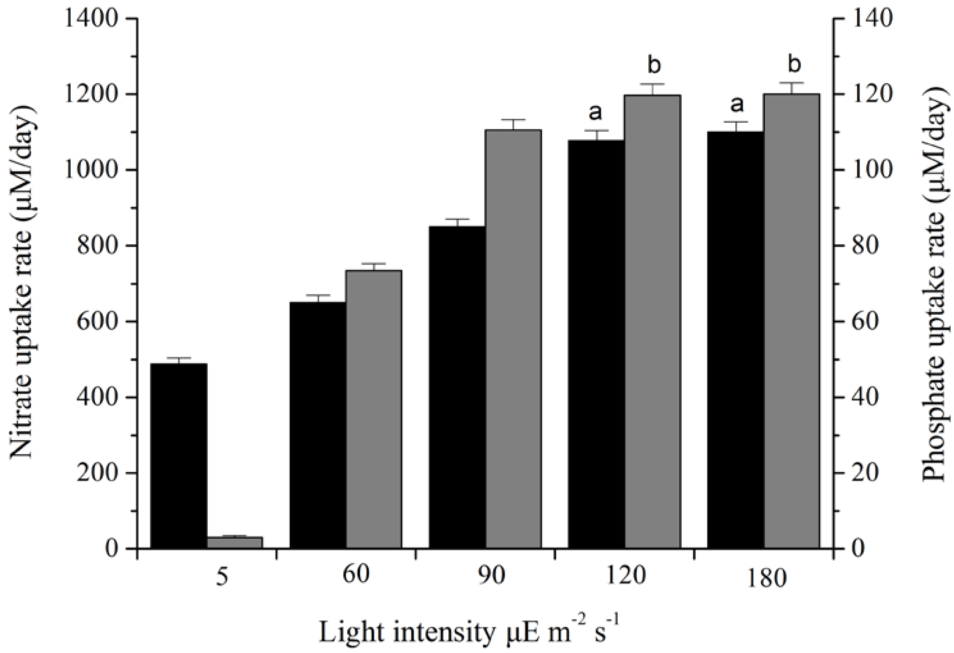


Figure 5. Influence of light intensity on nitrate (black columns) and phosphate (grey columns) uptake rates by co-immobilized algal cells of *Chlamydomonas reinhardtii* with graphene oxide. Bars represent ±1 SE. Means within a column for each treatment followed by the same letters do not differ significantly from each other.

3.1.4. Nitrate and phosphate uptake in fed-batch conditions

Alginate entrapped *C. reinhardtii* cells with graphene oxide were tested for nitrate and phosphate uptake over 5 cycles (Table 1). The average cell loading within the beads was 8 mg dry cells per g gel. Afterwards, five sequencing batches were performed with initial concentrations 1.5 mM NaNO3 and 0.15 mM KH_2PO_4 in every cycle.

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Table 1. Nitrate and Phosphate uptake rates and total consumption over five repeated cycles of co-immobilized algal cells of *Chlamydomonas reinhardtii* with graphene oxide. Means within a column for each treatment followed by the same letters do not differ significantly from each other.

Cycle	Uptake rate (μmole $g^{-1}d^{-1}$)		Total Consumption (mg L^{-1})	
	Nitrate	Phosphate	Nitrate	Phosphate
1	1485±40[a]	169±9	213±4	26±1
2	1406±60[a]	130±7	411±6	52±2
3	1509±15[a]	88±7	611±9	76±4
4	1375±30	50±6	803±18	91±5[b]
5	1250±27	23±6	987±32	94±5[b]

The nitrate consumption rates over the first, second and third periods were similar, decreasing slightly over the last two batches (about 80% in the fifth cycle). The total removal of nitrogen was reached 1000 mg L^{-1} after 5 cycles. The phosphate removal rates was 169±9 μmole $g^{-1}d^{-1}$ at the first cycle, decreased 25% at the second cycle and dropped continuously in the next cycles. The total removal of phosphorus at the end of the 5th cycle was 94 ±5 mg L^{-1}.

4. CONCLUSIONS

In conclusion, we have shown that calcium alginate-entrapped cells of *Chlamydomonas reinhardtii* in presence of graphene based nanomaterials, especially with graphene oxide, increases nitrate and phosphate uptake rates significantly. Co-immobilization of photosynthetic microalgae with nanomaterials in natural polymers could be an interesting tool to be applied in specific nitrate and phosphate removal processes. Furthermore, the overall process incorporates green chemistry principles in using naturally available resources, such as microalgae and graphite, for wastewater treatment, in removing all traces of nitrate and phosphate from liquid effluents, more efficiently than the alone microalgal cells.

References

[1] Olguin, E.J., 2003. Phycoremediation: key issues for cost-effective nutrient removal processes. *Biotechnology Advances*, **22**, 81 – 91.

[2] Oswald W.J., 1988. Micro-algae and waste-water treatment M.A. Borowitzka, L.J. Borowitzka (Eds.), Micro-algal Biotechnology, Cambridge University Press, 305 – 328.

[3] Mallick, N., Rai L.C., 1993. Influence of culture density, pH, organic acids and divalent cations on the removal of nutrients and metals by immobilized *Anabaena doliolum* and *Chlorella vulgaris*. *World Journal of Microbiology and Biotechnology*, **9**, 196 – 201.

[4] Trevan, M.D., Mak, A.L., 1989. Immobilized algae and their potential for use as biocatalysts. *Trends in Biotechnology*, **6,** 68–73.

[5] Wijffels, R.H., Buitelaar, R.M., Bucke, C., Tramper, J., 1996. Immobilized Cells: Basics and Applications, Elsevier, Amsterdam.

[6] Robinson, P.K., Mak, A.L., Trevan, M.D., 1986. Immobilized algae: a review. *Process Biochemistry*, **21**, 122 – 127.

[7] Kaya, V.M., de la Noüe, J., Picard, G., 1995. A comparative study of four systems for tertiary wastewater treatment by *Scenedesmus bicellularis*: new technology for immobilization. *Journal of Applied Phycology*, **7(1),** 85–95.

[8] Lau, P., Tam, N., Wong, Y., 1997. Wastewater nutrients (N and P) removal by carrageenan and alginate immobilized *Chlorella vulgaris*. *Environmental Technology*, **18(9),** 945–951.

[9] Eroglu, E., Agarwal, V., Bradshaw, M., Chen, X., Smith, S.M., Raston, C.L., Swaminathan, I.K., 2012. Nitrate removal from liquid effluents using microalgae immobilized on chitosan nanofiber mats. *Green Chemistry* **14(10),** 2682–2685.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas

ISBN: 978-960-6865-94-7

[10] Chen, Y.C., 2001. Immobilized microalga *Scenedesmus quadricauda* (Chlorophyta, Chlorococcales) for long-term storage and for application for water quality control in fish culture. *Aquaculture,* **195**, 71 – 80.
[11] Mallic, N., 2002. Biotechnological potential of immobilized algae for wastewater N, P and metal removal: a review. *BioMetals,* **15**, 377 – 390.
[12] Cohen, Y., 2001. Biofiltration – the treatment of fluids by microorganisms immobilized into the filter bedding material: a review. *Bioresource Technology,* **77**, 257 – 274.
[13] Jeanfils, J., Thomas, D., 1986. Culture and nitrite uptake in immobilized *Scenedesmus obliquus*. *Applied Microbiology and Biotechnology*, **24,** 417–22.
[14] Romo, S., Pérez-Martinez, C., 1997. The use of immobilization in alginate beads for long-term storage of *Pseudoanabaena galeata* (Cyanobacteria) in the laboratory. *Journal of Phycology,* **33,** 1073–6.
[15] Hertzberg, S., Jensen, A., 1989. Studies of alginate-immobilized marine microalgae. *Botanica Marina,* **32,** 267–73.
[16] Vílchez, C., Garbayo, I., Markvicheva, E., Galván, F., León, R., 2001. Studies on the suitability of alginate-entrapped *Chlamydomonas reindhartii* cells for sustaining nitrate consumption processes. *Bioresource Technology,* **78**, 55–61.
[17] Chevalier, P., De la Noüe, J., Wastewater nutrient removal with microalgae immobilized in carrageenan. Enzyme Microb Technol 1985;7:621–4.
[18] Chevalier, P., De la Noüe, J., 1985. Efficiency of immobilized hyperconcentrated algae for ammonium and orthophosphate removal from wastewaters. *Biotechnology Letters,* **6,** 395–400.
[19] Travieso, L., Benitez, F., Dupeiron, R., 1992. Sewage treatment using immobilized microalgae. *Bioresource Technology,* **40,** 183–7.
[20] Kaya, V.M., Goulet, J., De la Noüe, J., Picard, G., 1996. Effect of intermittent CO2 enrichment during nutrient starvation on tertiary treatment of wastewater by alginate-immobilized *Scenedesmus bicellularis*. *Enzyme and Microbial Technology,* **18,** 550–4.
[21] Yan, G., Yu, J., Wang, Y., 1996. The effects of pH and temperature on orthophosphate removal by immobilized *Chlorella vulgaris*. *Biotechnology Letters*, **18,** 893–6.
[22] Garbayo, I., Vigara, A.J., Conchon, V., Martins Dos Santos, V.A.P., Vilchez, C., 2000. Nitrate consumption alterations induced by alginate-entrapment of *Chlamydomonas reindhartii* cells. *Process Biochemistry,* **36**, 459–466.
[23] Sánchez, C.V., Jachak, A., Hurt, R.H., Kane, A.B., 2012. Biological interactions of graphene-family nanomaterials: an interdisciplinary review. *Chem. Res. Toxicol*., **25**, 15 – 34.
[24] Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., A.A. 2004. Firsov Electric field effect in atomically thin carbon films. *Science,* **306**, 666 – 669.
[25] Singh, Z., 2016. Document Applications and toxicity of graphene family nanomaterials and their composites. *Nanotechnology, Science and Applications,* **9,** 15-28.
[26] Wahid, M.H., Erogl,u E., Chen, X., Smith, S.M., Raston, C.L., 2013. Entrapment of *Chlorella vulgaris* cells within graphene oxide layers. *Royal Society of Chemistry Advances* **3(22)**, 8180 – 8183.
[27] Wahid, M.H., Eroglu, E., Chen, X., Smith, S.M., Raston, C.L., 2013.Functional multi-layer graphene–algae hybrid material formed using vortexfluidics. *Green Chemistry,* **15(3)**, 650-655.
[28] Pavlidis, I.V., Patila, M., Bornscheuer, U.T, Gournis, D., Stamatis, H., 2014. Graphene-based nanobiocatalytic systems: Recent advances and future prospects. *Trends in Biotechnology* **32(6),** 312 – 320.
[29] Harris, E.H., 1989. The Chlamydomonas sourcebook: a comprehensive guide to biology and laboratory use Academic Press, San Diego.
[30] Eijckelhoff, C., Dekker, J.P., 1997. A routine method to determine the Chlorophyll α, pheophytin *a* and beta-carotene contents of isolated Photosystem II reaction center complexes. *Photosynthesis Research,* **52**, 69–73.
[31] Diatloff, E., Rengel., Z., 2001. Compilation of simple spectrophotometric techniques for the determination of elements in nutrient solutions. *Journal Plant Nutrition,* **24**, 75 – 86.
[32] 4500-P E., Ascorbic acid method L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), 1998. Standard Methods for the Examination of Water and Wastewater (20th ed.), American Public Health Association, Washington, DC, **4,** 146-147.
[33] Vilchez, C., Vega, J.M., 1995. Nitrite uptake by immobilized *Chlamydomonas reinhardtii* cells growing in airlift reactors. *Enzyme and Microbial Technology,* **17,** 386–390.

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Protection and Restoration of Coastal Zone and Open Sea Waters

PROTECTION AND RESTORATION OF THE ENVIRONMENT XIII

Exploitation of wave energy while protecting the coast from erosion

I. Roupas*, **E. Sarivasileiou, T. Karambas**

Depaprtment of Civil Engineering, Aristotle University of Thessaloniki, 54124, Greece
*Corresponding author: Email: roupas.yan@gmail.com

Abstract

In the present work the effectiveness of applying a farm of Wave Energy Converter (WEC) with the simultaneous implementation of the beach nourishment method, for coastal protection against erosion, is numerically investigated. DEXA WEC was chosen as the most suitable for the present case study. A main aim is to obtain an 'optimal' design of each device and of the layout of the wave farm, in order to reduce the wave energy transmission. The simulation of the wave transformation behind the WEC farm, the breaking wave induced currents and the sediment transport, is based on existing numerical coastal hydro-morphodynamics models. The results of the models demonstrate the effects of the WEC farm on the reduction of the sediment transport that leads to coastal erosion and the effectiveness of the DEXA layout to protect the artificially nourished coast.

Keywords: Wave Energy Converters; DEXA; coastal protection

1. INTRODUCTION

Over the past decades the problem of coastal erosion has expanded and it is expected to be more intense as a result of the climate change and the sea level rise. The solutions used so far to confront this problem have been basically constituted of 'hard' and 'soft' conventional methods such as emerged and submerged breakwaters, groins etc, combined with the method of beach nourishment. However, even the 'soft' methods, which are considered environmentally friendly, are not able to face the expected sea level rise because they are becoming less efficient, while increasing the water level [1]. Additionally, the installation of breakwaters is in some cases inapplicable in terms of constructability and economically unprofitable.

The purpose of this paper is to examine whether a farm of Wave Energy Converters (WEC) combined with the method of beach nourishment can be applied instead of conventional methods in order to protect the beach "Vrahakia", in the coast of Itea, against erosion.

DEXA WEC was chosen as the most suitable device for the present case study. DEXA is a floating WEC that belongs to the Wave Activated Body (WAB) type, where the energy production is based on the relative movement of its components (www.dexawave.com). DEXA is an environmentally friendly device, since it has been designed in such a manner that sea animals cannot get squeezed, trapped or injured, while as a floating device does not prevent the circulation of waters. In addition, its hydraulic system uses water, which does not pollute the environment if there is a leakage [2].

A proper design of the method refers to the installation of a farm of Wave Energy Converters (WEC) combined with the method of beach nourishment, requires the use of existing advanced mathematical models [3], capable of simulating the complicated hydro-morphodynamic processes of the near shore region (including swash zone), such as wave propagation, wave-induced current, sediment transport by waves and currents and bed morphology evolution. The present coastal engineering model consists of several modules describing the wave field, the spatial distribution of

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wave-induced currents, the associated sediment transport fluxes, and, finally, the resulting spatial and temporal changes of the bed level. The model that is used in the present study consists of three main modules: WAVE-L, WICIR and SEDTR [3].

2. DEXA LAYOUT

DEXA device is a floating structure and its efficiency in protecting a coastal zone from erosion can be compared to that of a floating breakwater. These structures partially reflect and partially dissipate the incident wave energy, so that the wave transmission is significantly reduced, at least for wave periods smaller than the period considered for the design of the floating structure[4]. Unfortunately, they can be used for coastal protection purposes only where the wave climate is particularly mild [1].

It is clear that the energy absorbing effect of a WEC, such as DEXA, reduces the wave height at its leeward side. The amount of this reduction depends on the amount of absorption (absorption coefficient) and the geometry (length and width) of the WEC, as well as on the incident wave climate [5].

The aim of this study is the "optimal" design of the DEXA device and of the layout of the WEC farm for coastal protection purpose and for this reason the following guidelines [6], based on the experimental results obtained from experiments conducted at Aalborg University, DK [4][6][7] were taken into account:

A) The design of the device should consider that:
- The device's length, *l*, has to be 'turned' on the basis of the local peak wave length and, specifically, the condition *l*/L=1.0 (L: wave length corresponding to the peak period) has to be assured for most of the year, since it leads to the best compromise between wave transmission and power production performance.
- If other design features are kept constant, a heavier system gives a better result as far as the decrease of the incident wave energy.
- For oblique waves the transmission coefficient, K_T, decreases [4].

B) The farm layout should:
- Benefit from the interaction between the devices, that would be enhanced by reducing the gap width up to the minimum distance required (3b, b: device width) to let the devices and the moorings freely moving; the reduction in gap width leads also to an economic optimization of the farm layout, being less marine space required to deploy the devices for the same target energy production;
- Place the devices staggered-in cross-shore direction, so that the devices are still reached by a great amount of residual wave energy and again lead to a more compact layout;
- Be repeated along the cross-shore direction to provide an appreciable sheltering effect.

<u>Device Length</u>

The optimal length of the device is calculated according to the above guidelines, so that the ratio *l*/L (*l*: length of the device, L: wave length) will be close to or even bigger than 1.0 for the biggest part of one year period [6]. The "optimization process" focuses on South and South-West winds which are stronger and more frequent in the coast of Itea. Especially for the South-West wind, the *l*/L values for most wind intensities, reach and exceed the unit (Table 1), and in combination with the large wave steepness of South-West ripple due to the small footage spread and the strong winds, guarantee low values of the transmission coefficient, K_T.

The dimensions of the device are shown in Figure 1 below (l=30m, b=11m).

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Table 1: Ratio of *l*/L for S, SW and SE winds

	S	SW	SE
l /L	1.201009	1.559657	1.282983
	0.856531	1.250521	1.02522
	0.795798	1.029972	0.849425
	0.683356	0.882145	-
	-	0.68584	-
	0.489484	0.619579	-

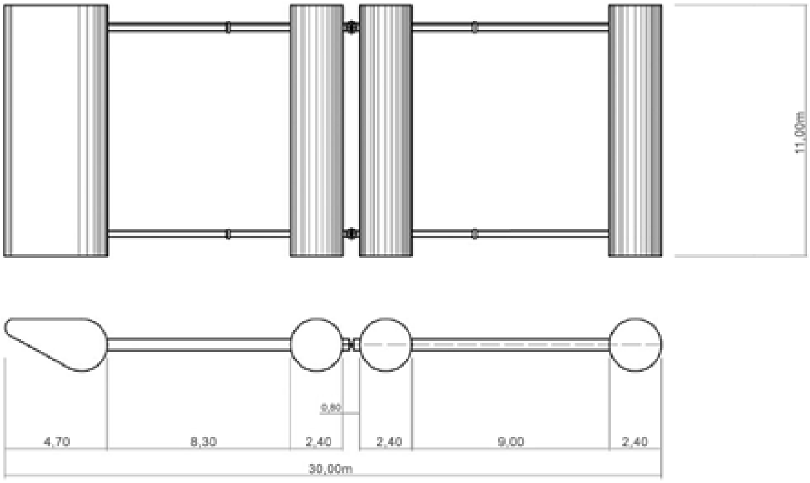


Figure 1. Dimensions of the DEXA device.

Installation angle

The results of a set of tests at Aalborg University show that there is a certainly reduction of wave transmission with increasing obliquity [4].

In order to minimize the value of the transmission coefficient, K_T, the orientation of the devise relative to the South direction is selected equal to 15 degrees. Therefore, the orientation of the device relative to the South-West direction is equal to 30 degrees (Figure 2).

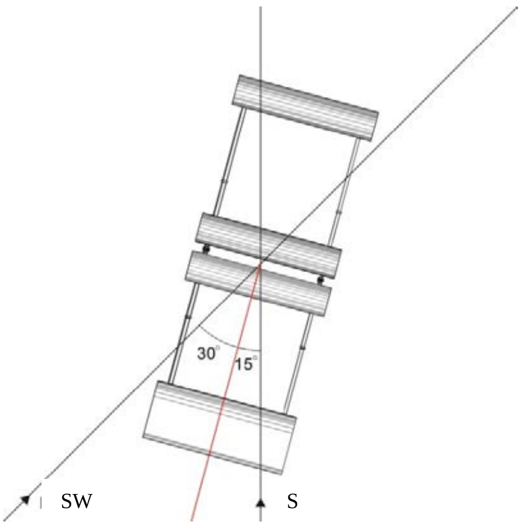


Figure 2. Installation angle of the DEXA device.

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Layout of DEXA farm

The results of the tests took place at Aalborg University combined with the results derived from Mike 21 [7] demonstrated that the influence of the device of the first row relative to the devices of the second row, completely disappears within a length equal to *l* (length) of the device. This distance between the devices of the first and second row is necessary because the wake of the devices of the first row could dramatically reduce the performance of the devices of the back line [7]. The distance between the DEXA devices in a row and the in-between distance of the rows will determine the total impact of the farm on the wave climate and on the surrounding users of the sea and it should be as small as possible to reduce also the cost of the farm [5].

Moreover, it was found that the gap between the devices within the farm is crucial for ensuring a reduced transmission coefficient, K_T. Specifically, the smaller the gap the greater the reduction of the incident wave energy, due to the phenomenon of diffraction and superposition of the diffracted waves. However, the safe distance between two devices of the same line is from 2.5 to 4 times the width of the device, so as to ensure that there will be no problem in the operation of the mooring systems [6].

Therefore, it is possible to reduce up to 40% the wave height which is transmitted from the «farm» of DEXA, achieving a transmission coefficient, K_T, of the order of 0.6.

So, in the case study of the coast of Itea (Figure 3), the distance between devices of the same line is selected equal to 3b, i.e. equal to 33m and the distance between the front and back line is selected equal to *l* = 30m. According to the above dimensions, a total of 31 devices of the same size and same efficiency is estimated to be placed in the areas, with 15 devices in the outer line and 16 in the inner line.



Figure 3. Farm of DEXA WEC and coast of Itea.

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3. MODELS DISCRIPTION

3.1 WAVE-L module

The module consists of the following hyperbolic-type mild slope equations:

$$\frac{\partial \eta}{\partial t}+\frac{\partial (U_W d)}{\partial x}+\frac{\partial (V_W d)}{\partial y}=0$$

$$\frac{\partial U_W}{\partial t}+\frac{1}{d}\frac{\partial (c^2 \eta)}{\partial x}-\frac{1}{d}\frac{g\eta}{\cosh (kd)}\frac{\partial d}{\partial y}= v_h \frac{\partial U_w^2}{\partial x^2}+v_h \frac{\partial U_w^2}{\partial y^2}-f_b \sigma U_W$$

$$\frac{\partial V_W}{\partial t}+\frac{1}{d}\frac{\partial (c^2 \eta)}{\partial x}-\frac{1}{d}\frac{g\eta}{\cosh (kd)}\frac{\partial d}{\partial y}= v_h \frac{\partial V_w^2}{\partial x^2}+v_h \frac{\partial V_w^2}{\partial y^2}-f_b \sigma U_W \quad (1)$$

where η is the surface elevation, U_w and V_w are the mean velocity along x and y directions, d is the water depth, c is the celerity, c=L/T, f_b a friction factor and v_h is a horizontal eddy viscosity coefficient [8] estimated [9]. The loss of energy due to the effects of breaking is introduced with a dispersion term in the right-hand side of momentum equations (Eq. 1).

The following boundary conditions are applied in the model:

(a) A sponge layer boundary condition, which is used to absorb the outgoing waves in the four sides of the domain [10].

(b) A total reflection boundary condition (U_w or V_w = 0) due to the existence of vertical structures is incorporated in the model.

(c) Partial reflection by introducing an artificial eddy viscosity coefficient, v_h.

3.2 WICIR (Wave Induced CIRculation) module

The loss of energy because of the wave breaking, combined with the influence of refraction and diffraction, leads to the creation of coastal wave currents.

For simulating near-shore currents in the coastal zone the depth- and shortwave-average two-dimensional (2D) continuity and momentum equation (Eq. 2) [8] are used.

$$\frac{\partial \zeta}{\partial t}+\frac{\partial (Uh)}{\partial x}+\frac{\partial (Vh)}{\partial y}=0$$

$$\frac{\partial U}{\partial t}+U\frac{\partial U}{\partial x}+V\frac{\partial U}{\partial y}+g\frac{\partial \zeta}{\partial x}=-\frac{1}{\rho h}\left(\frac{\partial S_{xx}}{\partial x}+\frac{\partial S_{xy}}{\partial y}\right)+\frac{1}{h}\frac{\partial}{\partial x}\left(v_h h\frac{\partial U}{\partial x}\right)+\frac{1}{h}\frac{\partial}{\partial y}\left(v_h h\frac{\partial U}{\partial y}\right)+\frac{\tau_{sx}}{\rho h}-\frac{\tau_{bx}}{\rho h}$$

$$\frac{\partial V}{\partial t}+U\frac{\partial V}{\partial x}+V\frac{\partial V}{\partial y}+g\frac{\partial \zeta}{\partial y}=-\frac{1}{\rho h}\left(\frac{\partial S_{xy}}{\partial x}+\frac{\partial S_{yy}}{\partial y}\right)+\frac{1}{h}\frac{\partial}{\partial x}\left(v_h h\frac{\partial V}{\partial x}\right)+\frac{1}{h}\frac{\partial}{\partial y}\left(v_h h\frac{\partial V}{\partial y}\right)+\frac{\tau_{sy}}{\rho h}-\frac{\tau_{by}}{\rho h} \quad (2)$$

where S_{xx}, S_{yy} and S_{xy} are the radiation stresses, ζ is the mean water surface elevation, h is the total depth (h= d+ζ), U, V are the current horizontal velocities and τ_{bx} and τ_{by} are the bottom shear stresses.

Radiation stresses are calculated from linear wave theory equations (Eq. 3) [11], without the assumption of progressive waves. Eq. 3 can be used for coastal areas where the waves are subjected to the combined effects of shoaling, refraction, diffraction, reflection (total and partial) and breaking.

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$$\frac{S_{xx}}{\rho} = d^2 < U_w^2 > A_r \text{-} d^2 < \left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)^2 > B_r + \frac{\partial}{\partial x} < \left[U_w\left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)\right] > D_r \; +$$

$$\frac{\partial}{\partial y} < \left[V_w\left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)\right] > D_r \; + \frac{1}{2} g < \eta^2 >$$

$$\frac{S_{yy}}{\rho} = d^2 < V_w^2 > A_r \text{-} d^2 < \left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)^2 > B_r + d^2 \frac{\partial}{\partial y} < \left[V_w\left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)\right] > D_r \; +$$

$$d^2 \frac{\partial}{\partial x} < \left[U_w\left(\frac{\partial U_w}{\partial x} + \frac{\partial V_w}{\partial y}\right)\right] > D_r \; + \frac{1}{2} g < \eta^2 >$$

$$\frac{S_{xy}}{\rho} = d^2 < U_w V_w > A_r \tag{3}$$

In a current model the treatment of the bottom stress is critical. In order to calculate the bottom shear stresses the total wave velocities at the bottom (u_b , v_b) are used. The expression for the time-average bottom shear stress in the current model is written below,

$$\tau_{bx} = \frac{1}{2}\rho f_{cw} < u_b \sqrt{u_b{}^2 + v_b{}^2} >$$
$$\tau_{by} = \frac{1}{2}\rho f_{cw} < v_b \sqrt{u_b{}^2 + v_b{}^2} > \tag{4}$$

where f_{cw} is the friction coefficient that depends on the bottom roughness and on the orbital amplitude at the bed.

3.3 SEDTR (SEDiment TRansport) module

The SEDTR module is used for the prediction of the sediment transport and, finally, for the calcualtion of the resulting spatial and temporal changes of the bed level. The submerged weight transport rates, q_{xt} in the x direction and q_{yt} in the y direction are given by [8],

$$q_{xt} = q_{bx} + q_{sx}$$
$$q_{yt} = q_{by} + q_{sy} \tag{5}$$

with

$$q_{bx} = \frac{1}{(\rho_s - \rho)g} < \left[\frac{\varepsilon_b}{\tan\Phi}\left(\frac{u_b}{u_{bt}} + \frac{d_x}{\tan\Phi}\right)\omega_b\right] > \quad , q_{sx} = \frac{1}{(\rho_s - \rho)g} < \left[\varepsilon_s \frac{u_{bt}}{w_f}\left(\frac{u_b}{u_{bt}} + \varepsilon_s d_x \frac{u_{bt}}{w_f}\right)\omega_t\right] >$$

$$q_{by} = \frac{1}{(\rho_s - \rho)g} < \left[\frac{\varepsilon_b}{\tan\Phi}\left(\frac{v_b}{u_{bt}} + \frac{d_y}{\tan\Phi}\right)\omega_b\right] > \quad , \; q_{sy} = \frac{1}{(\rho_s - \rho)g} < \left[\varepsilon_s \frac{u_{bt}}{w_f}\left(\frac{v_b}{u_{bt}} + \varepsilon_s d_y \frac{u_{bt}}{w_f}\right)\omega_t\right] >$$

where Φ is the angle of internal friction, ε_b and ε_s are the bed and suspended load efficiency factors, $u_{bt} = \sqrt{u_b^2 + v_b^2}$ ($u_b = u_b(t)$, $v_b = v_b(t)$ are the total flow velocities at the bottom), dx and dy are the bottom slopes, $\omega_b = < \frac{1}{2} f_{cw} \rho u_{bt}{}^3 >$ and ω_t ($\omega_t = \omega_b + D\, e^{3/2(1-h/H)}$) is the total rate of energy dissipation.

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The near-shore morphological changes are calculated by solving the conservation of sediment transport equation:

$$\frac{\partial d}{\partial t} = \frac{1}{(1-p)}\left(\frac{\partial q_{xt}}{\partial x} + \frac{\partial q_{yt}}{\partial y}\right) \tag{6}$$

where q_{tx}, q_{ty} are the volumetric long-shore and cross-shore sediment transport rates and p is the porosity of solids of the sediment (p≈0.4).

Table 1: Equivalent wave height H_e and wave period T_e on an annual basis.

Table 1			South wind			
BF	**U(m/s)**	**f %**	**H_{si} (m)**	**T_{pi} (sec)**	**H_e (m)**	**T_e (sec)**
4	6.7	2.988	0.58	3.51		
5	9.3	1.551	0.81	3.92		
6	12.3	0.787	1.07	4.32		
7	15.5	0.376	1.35	4.67	0.86	3.84
8	18.9	0.091	1.64	5.00		
9	22.6	0.011	1.97	5.31		
10	26.4	0.011	2.3	5.60		
Sum		5.815				

Table 2: Equivalent wave height H_e and wave period T_e on an annual basis.

Table 2			South-West wind			
BF	**U(m/s)**	**f %**	**H_{si} (m)**	**T_{pi} (sec)**	**H_e (m)**	**T_e (sec)**
4	6.7	1.106	0.71	4.00		
5	9.3	0.354	0.99	4.47		
6	12.3	0.114	1.30	4.92		
7	15.5	0.034	1.64	5.32	0.93	4.22
8	18.9	0.011	2.00	5.69		
9	22.6	0.000	2.39	6.04		
10	26.4	0.011	2.80	6.37		
Sum		1.630				

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Table 3: Equivalent wave height H_e and wave period T_e on an annual basis.

Table 3			South-West wind			
BF	**U(m/s)**	**f %**	**H_{si} (m)**	**T_{pi} (sec)**	**H_e (m)**	**T_e (sec)**
4	6.7	0.707	0.68	3.87		
5	9.3	0.080	0.94	4.33		
6	12.3	0.011	1.24	4.76	0.72	3.93
7	15.5	0.000	1.56	5.15		
8	18.9	0.000	1.91	5.51		
Sum		0.798				

4. APPLICATION

The above model was used in order to investigate the effectiveness of applying a farm of DEXA WEC combined with the method of beach nourishment. The study area is located near the city of Itea, Greece, at a coastal area named “Vrahakia”. In this coastal area we assume that the method of beach nourishment has been applied in order to create a sandy beach for recreation reasons.

Using the wind data from the specific area from the Greek Meteorological Service and applying the Jonswap wave prediction method the significant wave heights, H_s, the peak period, T_p, and the frequencies of the equivalent open sea waves were calculated.

The main incident wind directions are: South, South-West, and South–East. The equivalent wave height, H_e, (Table 1-2-3) on an annual basis is calculated according to [12] using the following expression:

$$H_e^{\,2}T_e = \frac{\Sigma H_{si}^2 T_{pi} f_i}{\Sigma f_i} \tag{7}$$

where, H_{is}, T_{pi}, f_i are the height, the period and the frequency of the waves that correspond on the various levels of wind intensity from each incident direction.

The following methodology has been adopted: First, the initial nourished bathymetry was introduced in the model and the wave and the wave induced current field is calculated. The results are used by the sediment transport model for the calculations of the sediment transport rates. Finally, the bathymetry was updated according to the sediment transport, by solving the conservation of sediment transport equation. This procedure was repeated until the state of equilibrium was reached or after a specific period.

4.1 Simulation of Dexa farm in the module

The loss of energy because of the DEXA WEC’s layout is simulated by introducing an artificial eddy viscosity coefficient, v_h, within the area in which the devices are placed (Figure 4). An appropriate value of the v_h coefficient was introduced in order to achieve reduction of incident wave heights and result to a transmission coefficient, K_T, of the order of 0.6.

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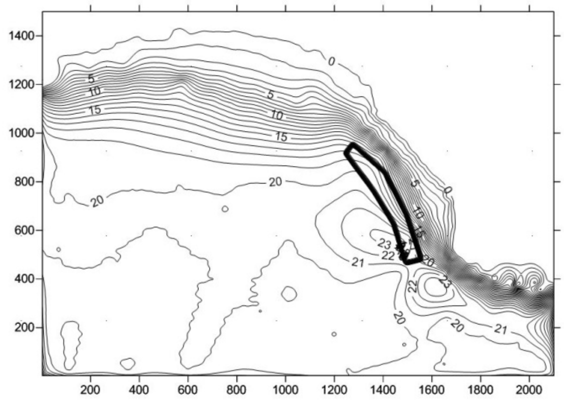


Figure 4. Area where partial reflection is introduced.

4.2. Model Results

In Figures 5 and 6 wave height and breaking wave induced current field is presented. The DEXA devices reduce the wave field and the intensity of the long shore currents, leading to the reduction of sediment transport and to the protection of the nourished coast. In Figure 7 the long-term bed morphology is shown, verifying the stabilization of the new nourished bathymetry and consequently the protection of the coast.

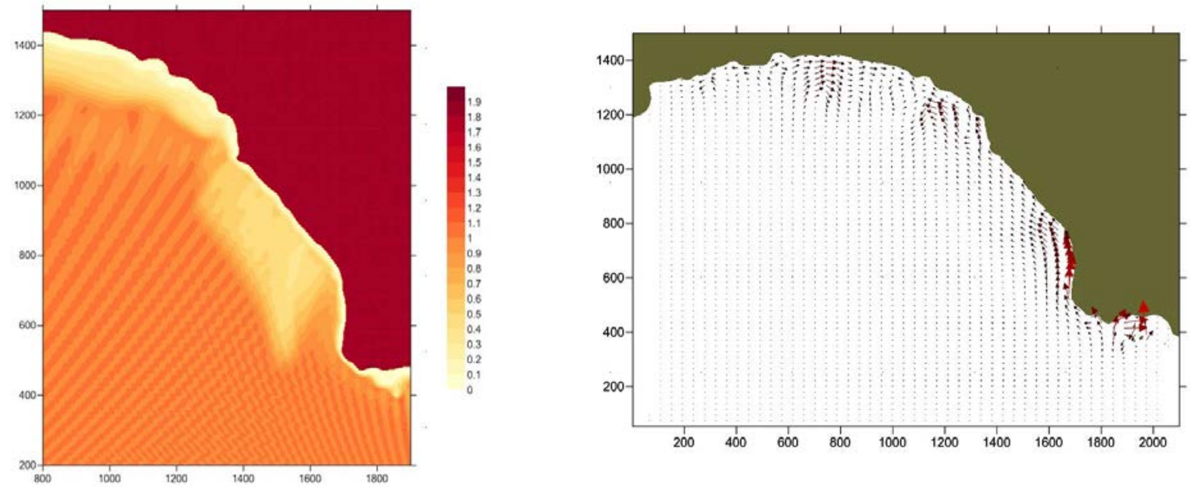


Figure 5. Wave height and wave induced circulation for South wind.

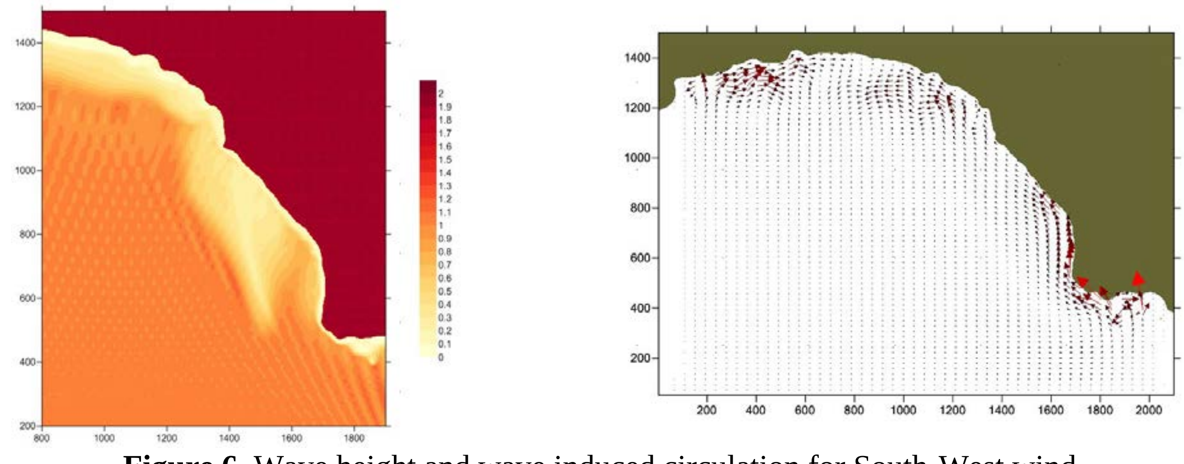


Figure 6. Wave height and wave induced circulation for South-West wind.

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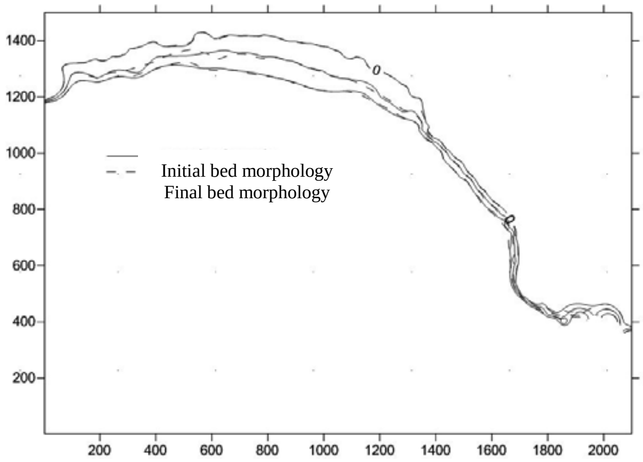


Figure 7. Long-term bed morphology evolution.

5. CONCLUSIONS

In the present work, the effectiveness of applying a WEC farm with simultaneous coastal protection from erosion is investigated. The DEXA WEC was chosen as the most suitable device, while the study area is located near the city of Itea, Greece. The results of the numerical models verify the effects of the WEC farm on the reduction of both the incident wave and the intensity of the longshore currents, even for relatively large transmission coefficient (of order of 0.6), leading to the reduction of sediment transport and to the protection of the nourished coast.

References

[1] Zanuttigh B., Martinelli L., Castagnetti M., Ruol P., Kofoed J.P. and Frigaard P., 2010. Integration of wave energy converters into coastal protection schemes. Proceedings of the 3rd International Conference on Ocean Energy, Bilbao.

[2] http://www.dexawave.com (accessed March, 2015).

[3] Karambas Th. V., E. Koutandos , N. Kampanis , 2013. *Numerical simulation of wave induced morphology evolution*, Proceedings of the ICE – Maritime Engineering, Volume 166, Issue 3, 01 September 2013, pages 113-124.

[4] Ruol P., Zanuttigh B., L. Martinelli , J. P. Kofoed , P. Frigaard , *Near-shore floating wave energy converters: Application for coastal protection*.

[5] Beels C., P. Troch, G. De Backer, M. Vantorre, J. De Rouck, *Numerical implementation and sensitivity analysis of a wave energy converter in a time-dependent mild-slope equation model,* 2010, Coastal Engineering 57 (2010), 471-492.

[6] Zanuttigh B., E. Angelelli , *Experimental investigation of floating wave energy converters for coastal protection purpose* , 2013, Coastal Engineering 80 (2013), 148-159.

[7] Angelelli E., Zanuttigh B., *A farm of wave activated bodies for coastal protection purposes* , Coastal Engineering, 2012.

[8] Karambas Th. V. (2002) *Modeling of sea-level rise effects on cross-shore coastal erosion*", Journal of Marine Environmental Engineering, vol. 7, pp. 15-24.

[9] *Battjes, J. A. (1975), Modelling of turbulence in the surf zone*, Proc. Symp. Modelling Technics, California, ASCE, pp 1050-1061.

[10] Larsen J. and Dancy H. , 1983, *Open boundaries in short wave simulations – a new approach.* Coastal Engineering 7(3): 285-297.

[11] *Copeland, G. J. M., (1985). Practical radiation stress calculations connected with equations of wave propagation,* Coastal Engineering, 9, pp 195-219

[12] Borah D.*K. and Balloffet A., "Beach evolution caused by littoral drift barrier", J. of Water*way, Port, Coastal and Ocean Eng., ASCE, vol 111, no4, 645-660, 1985.

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Experimental investigation of wave transmission and reflection at a system of low crested breakwaters

T. Giantsi*, C. I. Moutzouris

Laboratory of Harbour Works, School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou7, Zografou 15780, Greece.
*Corresponding author: Email: dgiantsi@central.ntua.gr

Abstract

Low crested breakwaters are used to protect beaches from wave action. A series of large scale 3D laboratory experiments were carried out to investigate the effects in wave characteristics (disturbance) around a system of two non-parallel, permeable, low crested breakwaters by oblique wave incidence. The transmission and reflection coefficients were calculated and compared to existing formulae. The existing formulae, for both phenomena, transmission and reflection, had good relation in some cases. The angle of wave incidence did not show important influence for the wave transmission while is affected the wave reflection. The influence of wave period must be investigated in wave transmission and the influence of wave height in wave reflection.

Keywords: wave transmission; wave reflection; low crested breakwater; physical model.

1. INTRODUCTION

Systems of Low Crested Structures (LCS) are used to protect and to restore eroded beaches. Functional design of low crested breakwaters requires an accurate prediction of wave transmission and set up in the sheltered area. The wave reflection is a secondary consequence from the construction of the structure at the non-protected sea area. The hydrodynamics around LCS's is complicated. The phenomena of shoaling, diffraction, wave breaking, wave penetration through the openings, wave overtopping e.t.c. affect the wave climate especially in the sheltered area. Many series of 2D wave tests were carried out in the past, to investigate both phenomena transmission and reflection. In this paper experimental data of 3D tests, of a system of two low crested breakwaters, non parallel to the shore, are presented and compared to existing formulae. In some cases experimental results had surprising good relation to the empirical formulae, as the design of the structures was complicated and other phenomena affect the collected data.

2. WAVE TRANSMISSION AND WAVE REFLECTION

2.1 Wave transmission at rubble mound LCS

Wave transmission is defined by the transmission coefficient K_t, which is the ratio of the transmitted to the incident significant wave heights (e.g. H_t and H_i) and represent the transmitted energy from the open sea to the sheltered area between the breakwater and the shoreline.

$$K_t = \frac{H_t}{H_i} \quad \textbf{(1)}$$

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The estimation of this coefficient is crucial in the design of the protecting structures. For this reason, many formulae are developed, based on 2D physical models and are used in engineering practice, with their own limitations.

A series of large scale 3D laboratory experiments were carried out to investigate the effects in wave characteristics (disturbance) around a system of two non-parallel, permeable, low crested breakwaters, by oblique wave incidence. In this study we will present the comparison of the results obtained by the previous experiments t the formulae developed by Van der Meer and Daemen [1] and d' Agremond et al. [2], in accordance with the reanalysed formula [3].

The main parameters describing wave transmission are:

H_i = the incident significant wave height, at the toe of the structure
H_i = the transmitted significant wave height, at the sheltered area
T_p = the peak period
s_{op}= $2\pi H_i/(gT_p^2)$, the wave steepness
h_c = the structure total height
B = the crest width
R_c= the freeboard
D_{n50} = the mean diameter of the armour rock
$\tan\alpha$ = the slope of the structure(seaward)
ξ_{op} = $\tan\alpha / (s_{op})^{0.5}$, the Iribarren parameter

The following equation is proposed by Van der Meer and Daemen, for traditional breakwaters:

$$K_t = a\frac{R_c}{D_{n50}} + \beta \qquad \textbf{(2)}$$

where

$$a = 0.031\frac{H_i}{D_{n50}} - 0.24 \quad \text{and} \quad \beta = -5.42 s_{op} + 0.0323\frac{H_i}{D_{n50}} - 0.0017\left[\frac{B}{D_{n50}}\right]^{1,84} + 0.51$$

The following equation is proposed by d' Agremond et al., for submerged and low crested breakwaters:

$$K_t = -0.4\frac{R_c}{H_i} + 0.64\left(\frac{B}{H_i}\right)^{-0.31}(1 - e^{-0.5\xi}) \qquad \textbf{(3)}$$

$0.075 \le K_t \le 0.75$ and $0.075 \le K_t \le 0.8$ for Eqs (1) and (2) respectively.

An improved formula is proposed for $B/H_i > 10$, for smooth structures, as follow:

$$K_t = -0.35\frac{R_c}{H_i} + 0.51\left(\frac{B}{H_i}\right)^{-0.65}(1 - e^{-0.41\xi}) \qquad \textbf{(4)}$$

2.2 Wave reflection at rubble mound

Wave reflection was not considered to be an important factor especially for rubble mound structures and only recently is under investigation. The wave reflection is defined by the reflection coefficient K_r, which is the ratio of the reflected to the incident significant wave heights (e.g. H_r and H_i) or the square root of the reflected energy to the incident wave energy (E_r, E_i.)

$$K_r = \frac{H_r}{H_i} = \left(\frac{E_r}{E_i}\right)^{1/2} \qquad \textbf{(5)}$$

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The comparison of the experimental data is chosen to be done with the formulae proposed a) by Muttray et al. [4] and b) by Zanuttigh and Van der Meer [5]. The Mutrray et al. formula depends only from the relative depth d/L_{op} where:

d = the depth at the toe of the structure

$L_{op} = gT_p^{\ 2} / 2\pi$, the wavelength according to the peak period T_p

The proposed formula by Mutrray et al. is:

$$K_t = 1/\left[1.3 + 6\pi\left(d / L_{op}\right)\right] \quad \textbf{(6)}$$

The proposed by Zanuttigh and Van der Meer formula is:

$$K_t = \tanh(\mathrm{A} - \xi_o^{\ \mathrm{B}}) \quad \textbf{(7)}$$

(7)

Where : A=12 and B=0.87

3. EXPERIMENTAL SET-UP

A 3 D physical model of two low crested breakwaters was constructed in a wave basin at the Laboratory of Harbour Works, National Technical University of Athens to investigate the protection and restoration of a beach under a geometrical scale of 1:40. To investigate the hydrodynamic performance of the breakwaters only, modification were done to isolate the response of the beach. A absorbing rip-rap was constructed. Each breakwater was 2.50 m long. The azimuth of the breakwater's axis were 8^o and 350^o for B1 and B2 respectively. Then wave measurements were conducted under oblique wave attack to calculate the transmission and reflection coefficients at the two breakwaters. The angle of the wave incidence had a 300^o azimuth. For the needs of this study 15 wave gauges were used. The layout of the experiments and the locations of the wave gauges are presented at Figure1. The transmission coefficient is calculated in the middle of the each breakwater, where H_t and H_i are the measured wave heights behind and in front of the breakwater respectively. The reflection coefficient is calculate, in front of the breakwaters, at the middle of them, using 4 wave gauges. Typical cross section of the experimental set-up in the wave basin is presented in Figure 2.

For the reproduction of the waves, a 3 paddles wave generator was used, producing JONSHAP type spectra with a peak enhancement factor of 3.3. Resistive type wave gauges and sound sensors collected wave data under a 50Hz sampling rate throughout the entire 600 sec duration of each test.

Measurements carry out for 8 different wave peak periods, from T_p=0.48 sec to T_p= 1.52 sec in model, at three different water depths. For each wave period from 1 to 3 wave heights were tested. Waves from the 3 higher periods were broken seaward the breakwaters. Totally 72 tests were conducted. The geometrical parameters of the breakwaters B1 and B2 are presented at Table 1. Wave measurements were analysed using "HR Wave Data"- Data Acquisition and analysis software program with Fast Fourier Transformation method. Wave spectral and statistical parameters were obtained.

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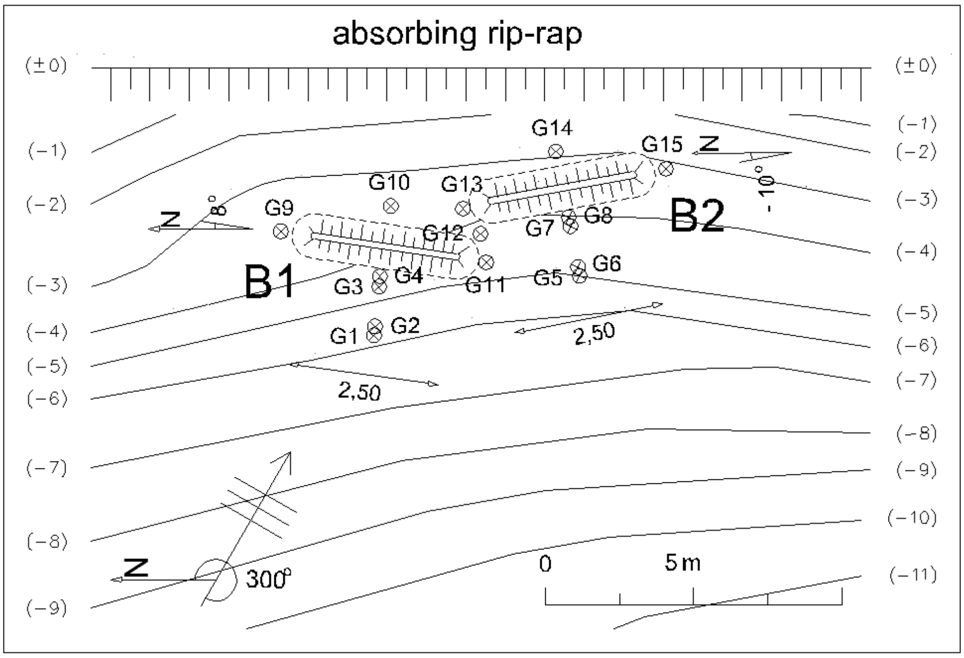


Figure 1. Layout of the physical model and locations of wave gauges

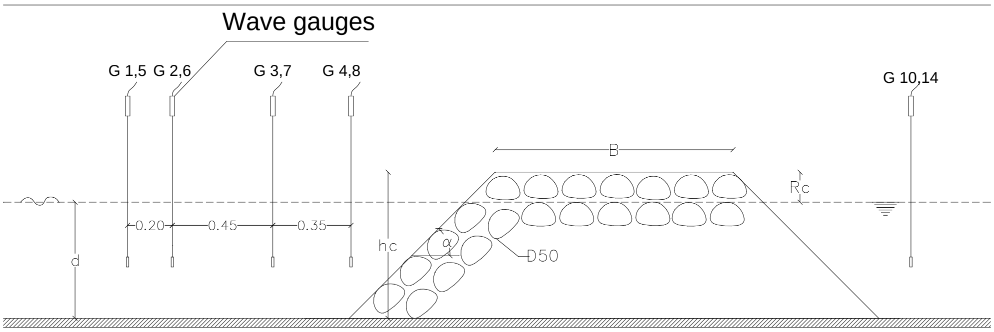


Figure 2. Typical cross section of the experimental set-up

Table 1. Geometrical parameters of Breakwaters B1 and B2

Data set	Wave direction (°)	B (mm)	hc (mm)	Rc (mm)	d (mm)	tan α	D_{n50} (mm)
B1.1	22	112.5	153	55	98	2.5	30
B1.2	22	112.5	153	35	118	2.5	30
B1.3	22	112.5	153	15	138	2.5	30
B2.1	40	112.5	138	50	88	2.5	30
B2.2	40	112.5	138	30	108	2.5	30
B3.3	40	112.5	138	10	128	2.5	30

4. DATA ANALYSIS - RESULTS

4.1 Wave transmission

The freeboard of the structure play an important role at the system performance, for this reason is chosen as the main parameter. For each data set the transmission coefficient K_t is calculated and plotted versus the relative freeboard R_c/H_i at the toe of the structure. To compare the performance of each breakwater it is plotted also the transmission coefficient of B1 versus the transmission coefficient of B2. (See Figure 3a and 3b). From Figure 3a it is observed that for $R_c/H_i>4$ the transmission coefficient is stable ~0.2. From both figures 3a and 3b it is observed that in most cases the transmission coefficient of B2 is lower than K_t of B1. It is noted that the crest of B2 is lower than the crest of B1. That may occur because B2 is in the shadow of B1 during this direction of wave incidence. Only in higher values of the transmission coefficient at the sheltered area of B2 is higher that these at B1.These values are observed in small relative freeboards and the protection by the B1 to the B2 is limited.

Next step is the comparison of the measured transmission coefficient, to the formulae proposed by a)Van der Meer and Daemen and b) d'Agremond et al. During the analysis, it is observed that, d' Agremond et al. formula produces many negative values and underestimates the values of K_t measured. According to the formula exists a lower limit, arbitrary proposed. The formula was developed analysing data from submerged breakwaters mainly. To validate the results, the relative errors were calculated (measured values minus calculated values) for both formulas, taken account the negative values and plotted versus the relative freeboard (See Figure 4).

From Figure 4 it is observed a systematic linear error for the d' Agremond et al. formula with the parameter R-squared = 0.945 (absolute linearity). To investigate the error, they were plotted the transmission coef. (measured and calculated) and relative errors versus relative freeboard, for $R_c/H_i<0.70$ and for $R_c/H_i>0.70$ respectively (See Figure 5a and 5b).

Relative errors, for both sub-datasets and the total dataset indicate that not significant differences between the slope of the trend line and the constant value obtained by the analysis. The only difference was at the R^2, with an acceptable level of errors when $R_c/H_i<0.70$. As is was observed the exponential factor of the formula was correct. The relative freeboard's factor of the formula, was corrected by introducing the function of the error and the modified - corrected formula d' Agremond et al., reads:

$$K_t = -0.0391\frac{R_c}{H_i} + 0.64\left(\frac{B}{H_i}\right)^{-0.31}(1-e^{-0.5\xi}) + 0.1072 \tag{8}$$

The influence of the relative freeboard in Equ. (8) is very small. The transmission coefficient K_t is recalculated according to Equ. (8). The measured and calculated values of the transmission coefficient versus the relative freeboard are presented in Figure 6a. At Figure 6b the calculated values versus the measured values of K_t are plotted.

As it is observed Van der Meer and Daemen formula has a very good agreement with the measured values especially when the relative freeboard is high ($R_c/H_i> 4$). For broken waves seaward the breakwaters, and for low freeboards the Van den Meer formula underestimates the phenomenon. The corrected d' Agremond formula has a very good agreement, with the measured values, at low relative freeboards ($R_c/H_i< 4$). The Equ. (8) must be validated by other experiments. The angle of wave incidence doesn't seems to play an important role in wave transmission. The highest values of K_t were observed with small relative freeboars and waves broken seaward the structures. The relative depth as a new factor may be introduced to the formulae.

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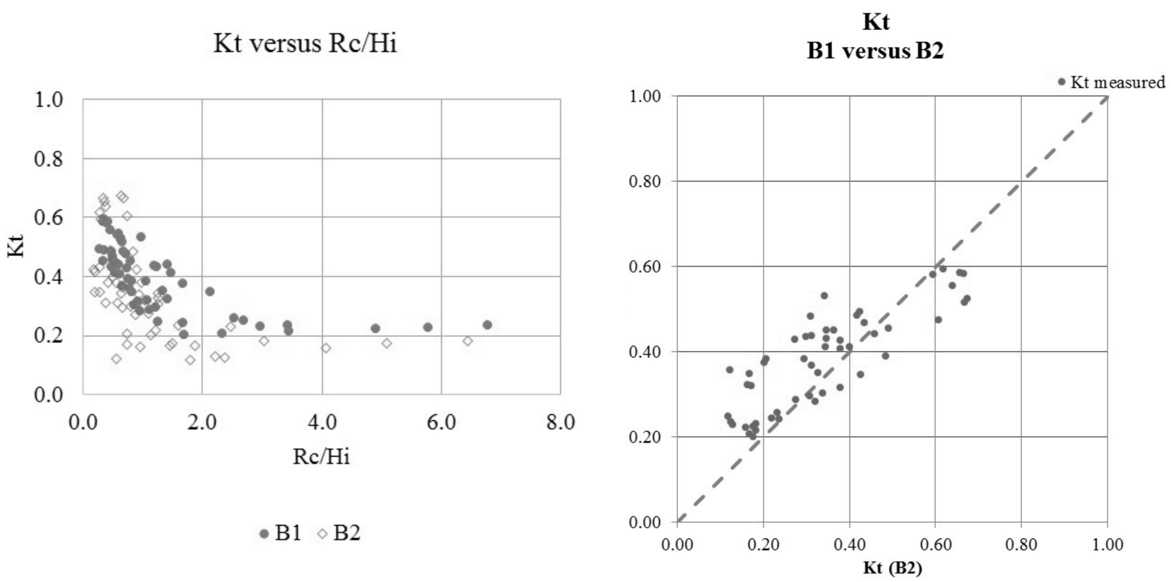


Figure 3. a) Transmission coefficient a) versus relative freeboard b) of B1 versus B2

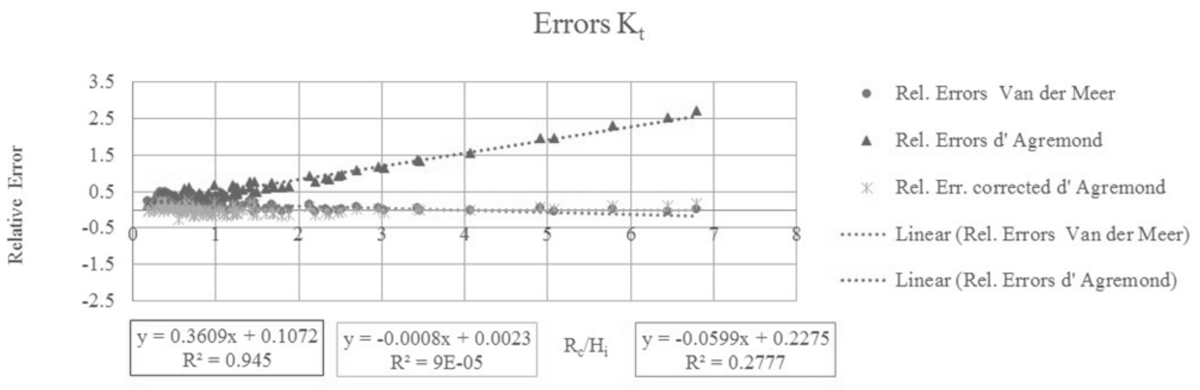


Figure 4. Relative errors of transmission coefficient versus relative freeboard

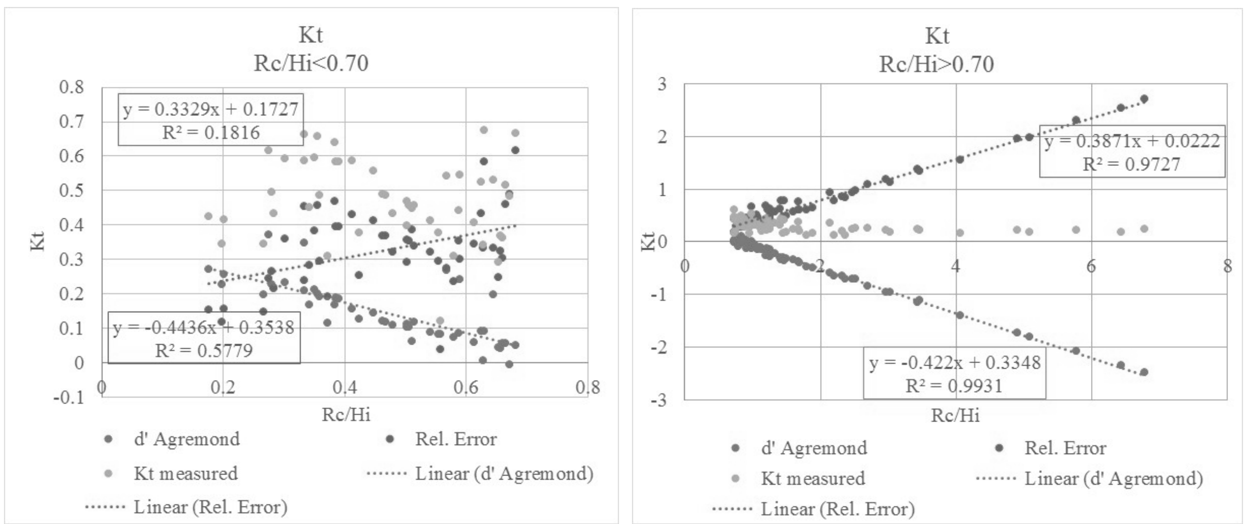


Figure 5. Relative errors and transmission coefficient versus relative freeboard a) for R_c/H_i<0.70 and b) for R_c/H_i>0.70

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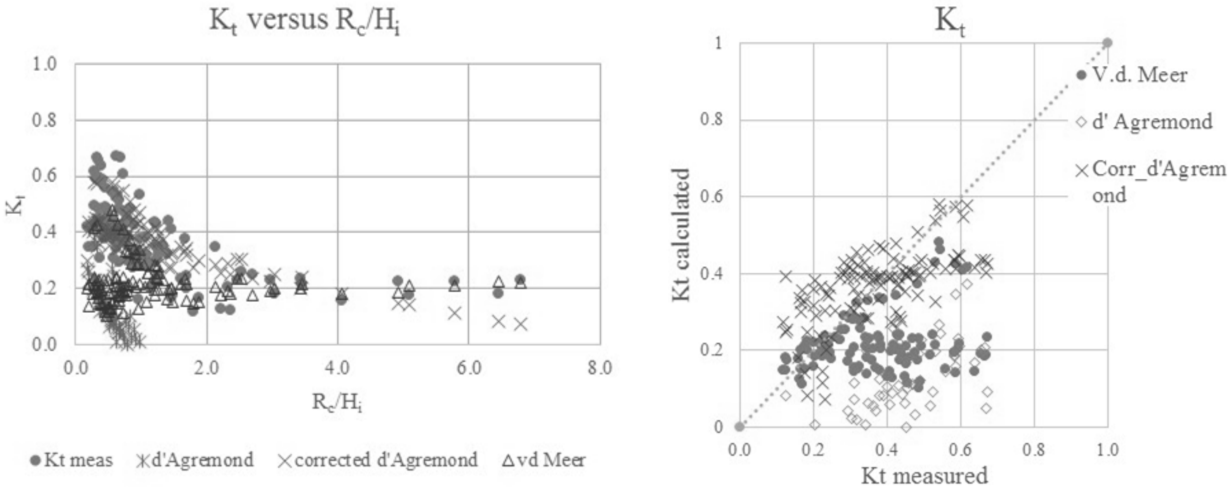


Figure 6. a) Transmission coefficient versus freeboard b) Calculated versus measured transmission coefficient

4.2 Wave reflection

For each data set the reflection coefficient is calculated using 4 wave gauges, as it is described by the appropriate routine of "HR Wave Data"- Data Acquisition and analysis software program. The wave reflection at rubble mound structures, was correlated to Iribarren parameter (ξ_o) and to relative freeboard. The Zanuttigh and Van der Meer formula is a simple formula correlating the Iribarren parameter to the wave reflection in front of a rubble mound structure. In contrary Myttray et al. correlated the reflection coefficient to the relative depth, totally independent of the wave height. The reflection coefficient (measured in front of B1 and B2 and calculated by both previously mentioned formulae) are plotted at Figure 7a) versus the relative freeboard and b) versus the Iribarren parameter. From Figures 7a and b is observed that the Zanuttigh and Van der Meer formula underestimates the measured reflection coef., especially for $R_c/H_i<1.0$. For $R_c/H_i>1.0$ the estimation is better. The Muttray et al. formula overestimates measured values for $R_c/H_i>1.0$ and estimates well measured values for $R_c/H_i<1.0$. At Figure 8a the measured values for B1 versus the measured values for B2 are plotted. Due to the very large dispersion of the measured values versus the Iribarren parameter, it is chosen to investigate the relative errors of the formulae. Furthermore breakwater B2 seems to be more reflective than B1, due to the different wave attack. Relative errors of the calculated values are plotted versus the main parameters concerning each formula (See Figure 8b and c).

From Figure 8a it is clear that the wave reflection is depending on the incidence angle of the waves. Relative errors from Muttray et al. formula, are symmetrical distributed, with a small constant value at the linear trend line of the errors, so this formula can be used and furthermore can be corrected. At the correction is not introduced the angle of the wave incidence. That will be the next step of our research. On the other hand relative errors from Zanuttigh and Van der Meer formula are not symmetrical distributed and any intervention has no meaning. The reflection coefficients (measured and calculated) versus the relative depth are presented in Figure 9a. The calculated versus the measured reflection coefficient is presented in Figure 9b.

As shown in Figures 9a and 9b, the Mutrray et al. formula and the corrected one, are very well correlated to the measured values of the reflection coefficient. The corrected formula gives better correlation between measured and calculated values, when the relative depth is greater than 0.10. For $0.05 < d/L_{op} < 0.10$ is observed the maximum deviation between the measured and calculated values. This formula doesn't take into account the relative freeboard who seems to be needed for the amelioration of the formula. The Zanuttigh and van der Meer formula underestimates the wave reflection, especially for low relative freeboards.

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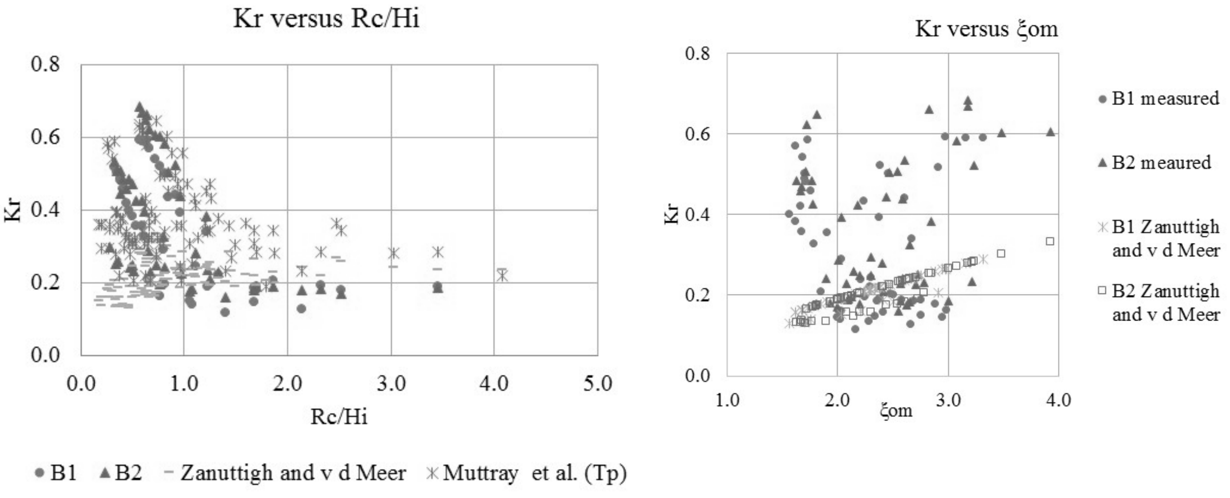


Figure 7. Reflection coefficient versus a) the relative freeboard b) the Iribarren parameter

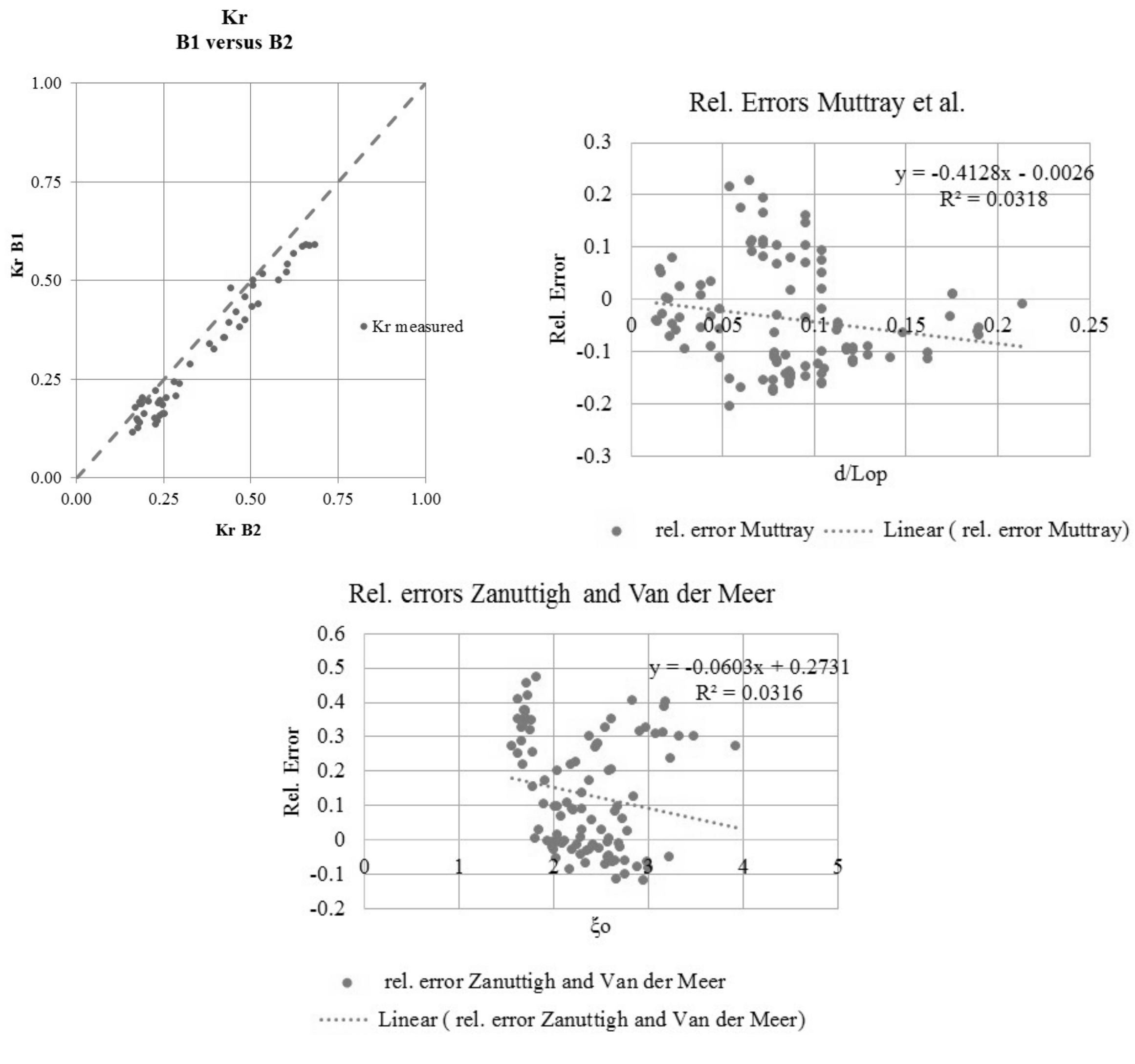


Figure 8. a) Measured reflection coefficients of B1 versus B2, a) Relative errors from Muttray et al. formula b) relative errors from Zanuttigh and Van der Meer formula

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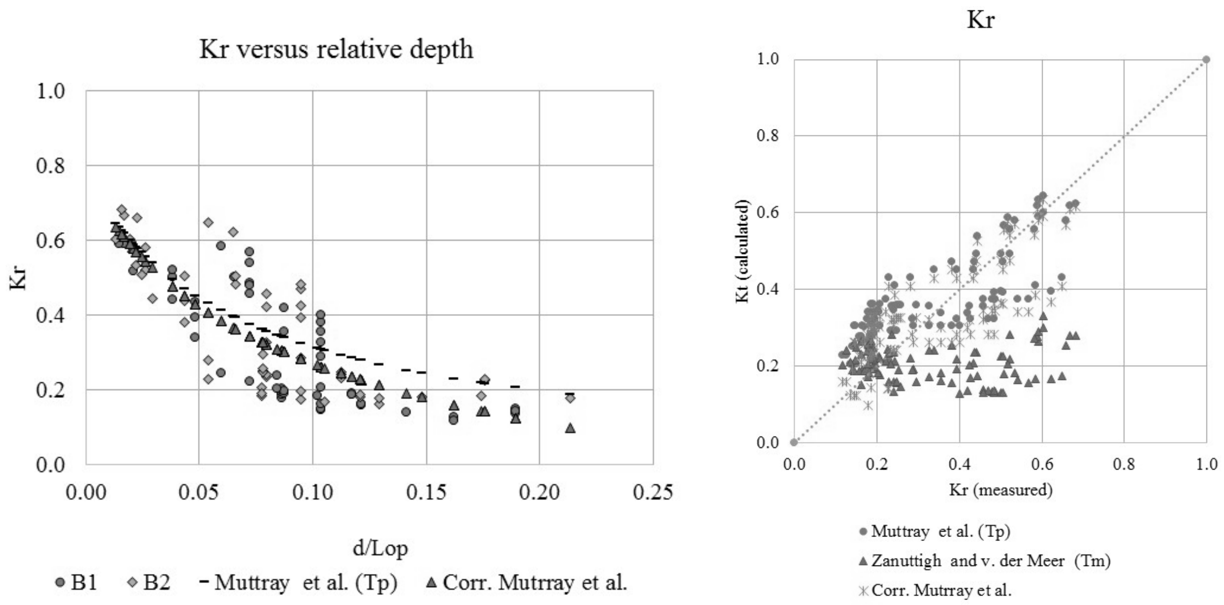


Figure 9. a) Reflection coefficient versus relative depth
b) Calculated versus measured reflection coefficient

5. CONCLUSION

In conclusion main results are:
The angle of the wave incidence does not affect the wave transmission significantly, while affects the wave reflection and must be further investigated. As it concern the transmission coefficient, is very well estimated by the Van der Meer et Daemen formula for relative freeboards greater than 4.0. The corrected d’ Agremond formula must be used for lower relative freeboards. The influence of the wave period must be investigated. As it concern the reflection coefficient, the proposed by Muttray et al. formula gives a very good initial estimation. The influence of the wave height must be investigated. Zanuttigh and van der Meer formula underestimates the reflection especially for relative freeboards greater than 1.0. The zone of structures with relative freeboard between 0 and 2 is a transitional zone, where the phenomena of wave transmission and wave reflection are very sensitive to many parameters.

References

[1] Van der Meer J.W., Daemen, I.F.R., 1994, Stability and wave transmission at low crested rubble mound structures, *Journal of waterway, Port Coastal and Ocean Engineering*, **1,** 1-19.
[2] D’ Angremond, K.,van der Meer, J.W., de Jong, R.J., 1998, Wave transmission at low-crested structures, *Proceedings of International Conferences of Coastal Engineering, ASCE*, 2418-2426
[3] Van der Meer J.W., Briganti R., Zanuttigh B., Wang B., 2005, Wave transmission and reflection at low-crested structures: Design formulae, oblique wave attack and spectral change on *Coastal Engineering*, **52**, 915-929.
[4] Muttray M., H. Oumeraci H., E. ten Oever, 2006, Wave reflection and wave run-up at rubble mound breakwaters, *International Conference on Coastal Engineering*, San Diego.
[5] Zanuttigh B., Van der Meer, J.W., 2008, Wave reflection from coastal structures in design conditions, *Coastal Engineering* **55**, 771-779.

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Preliminary results of seawater quality measurements at the New South Port of Patras, Greece

A. F. Aravantinou, A. Bloutsos, V. Tsiboukis, I. Manariotis, P. C. Yannopoulos*

Environmental Engineering Laboratory, Department of Civil Engineering,
University of Patras, 26504, Patras, Greece.
*Corresponding author: Email: yannopp@upatras.gr

Abstract

The Environmental Engineering Laboratory of the Civil Engineering Department of the University of Patras in cooperation with the Patras Port Authority SA carried out a monitoring program of seawater quality. Seven sampling campaigns were conducted from October 2013 until December 2014 at four sampling sites, in order to evaluate the contribution of surface runoff and harbour activities in seawater pollution. At each site, water quality parameters were determined in situ, and water samples were transferred and analyzed at the laboratory. Taking into consideration the whole set of measurements, it is concluded that the seawater quality of the port is satisfactory in comparison to other coastal zones of the major area of Patras and other ports. The increased concentration of microbiological parameters is attributed to the disposal of wastewater into the sea.

Keywords: port; seawater quality; physicochemical characteristics; heavy metals; microbiological characteristics

1. INTRODUCTION

The New Port of Patras is placed at the SW side of the Patras City and SE shoreline of Patraikos Gulf between the rivers Diakoniaris and Glafkos. The New Port has been in operation since July 2011. Up to the decade of 1980, along the Patras shoreline, south the Cathedral Church of Ag. Andreas, more than two hundrends of industries had been installed and operated, which discharged mainly raw wastewater into the Patraikos Gulf. Since the decade of 1990 and then, most of these factories were relocated in the Industrial Area of Patras, 20 km south approximately. Nowadays only a distillery is operating at the New Port neighborhood. However, the streams of Diakoniaris and Glafkos receive and transport wastewater from households and other activities, which are allocated along these rivers.

The development of the New Port of Patras consists of two phases. The 1st phase has a platform of total length of 992 m, built with caissons of reinforced concrete in a zigzag line. It consists of four side-mooring docks. It is approaching to be completed, since the three docks are already in operation and the last dock is under construction. The breakwater of the Port is 1,236 m in total length, built with caissons of reinforced concrete. The building infrastructure of the Port has a total coverage area of 6,974 m^2, which includes the terminal passenger station, the Port Administration building and a substation building, the Fire Station and other. The port serves maritime transport between Patras and Ionian Islands and Italy. A monitoring program of the seawater quality had been assigned by the Technical Department of the Patras Port Authority S.A. to the Environmental Engineering Laboratory of the Civil Engineering Department of the University of Patras. The program started on October 2013 and finished on January 2015, and seven campaigns were carried out (Table 1).

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Table 1. Monitoring Campaigns Schedule.

Campaign Number	1st	2nd	3rd	4th	5th	6th	7th
Date	25/10/2013	10/2/2014	12/4/2014	11/6/2014	26/8/2014	30/10/2014	10/12/2014

2. MATERIALS AND METHODS

2.1 Monitoring Area

After an exploratory visit at the monitoring area, the sampling sites A, B, C, D and E were determined (Figure 1). Site A was between docks of the New Port of Patras and the breakwater; Site B was at the discharge point of the South outlet of the collecting storm water conduit and the Sites D and E were at the two rivers discharging at both sides of the port, namely Glafkos R. and Diakoniaris R., respectively, in order to evaluate the contribution of surface runoff and harbor activities in the seawater pollution. Site C was a manhole of South collecting storm water conduit. The visit at this site showed that the flow inside the manhole was insignificant; thus, no samples were collected.

2.2 Physicochemical parameters

The Standard Methods for the Examination of Water and Wastewater [1] were followed at sampling procedures and measurements of physicochemical parameters. Especially for the examination of soluble heavy metals in seawater samples the proposed methods for seawater analysis of [2] were followed.

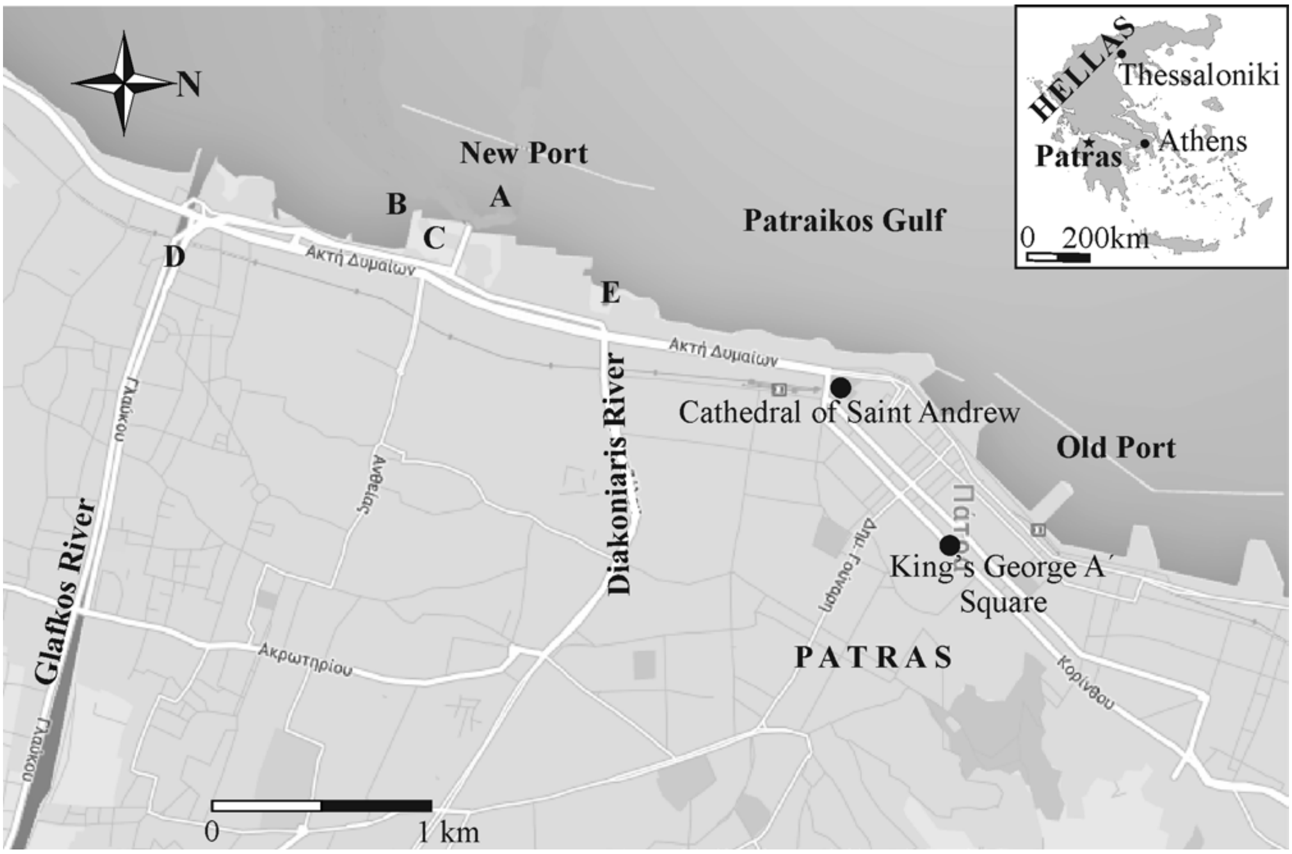


Figure 1. Map of the sampling area. Sampling Sites: A=Inside the New Port of Patras between docks and the breakwater, B=Discharge point of the South outlet of the collecting storm water conduit, C=Manhole of the South outlet of the collecting storm water conduit, D=Bedside of Glafkos River, E=Discharge Point of Diakoniaris River. (Source: www.google.maps.com)

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The water temperature (T_{water}), *pH*, dissolved oxygen (*DO*), electrical conductivity (*EC*) and turbidity (*TU*) were determined immediately after the sample was collected or directly by immersing into the water the appropriate probe. In addition, the water clarity of the seawater was measured using a Secchi disk. A mercury thermometer of 0.1°C gradation was used for the determination of air temperature. *pH* was measured using the pH-meter HI 8424 by HANNA Instruments. Similarly, electronic devices HANNA Instruments HI 98188 and YSI 85 were used at the determination of EC. *TU* was measured using the Turbidimeter HACH 2100AN IS. *DO*, *EC*, *salinity* and T_{water} were measured directly in the water using the YSI 85.

The determination of the concentrations of lead (*Pb*), copper (*Cu*) and arsenic (*As*) was made using flameless atomic absorption spectrophotometry. The model 2280 Perkin-Elmer spectrophotometer equipped with an HGA-300 graphite furnace and suitable hollow cathode lamps was used for all analytical measurements. The seawater samples (Sites A, B and E) were treated and measured according to [2]. The water samples from Glafkos R. (Site D) were collected and measured according to [3].

The determination of biological oxygen demand (BOD_5) was made according the procedure that is proposed by [1]. Similarly, total organic carbon (*TOC*) concentrations were measured according to [1] using a total organic carbon analyzer (Model TOC-5000, SHIMADZU).

Total nitrogen concentrations (*Total-N*) were determined by 2,6-Dimethylphenol spectrometric method [4]. Total phosphorus (Total-P) measured using the persulfate digestion και ascorbic acid method [1], and the *Chlorophyll-a* concentrations was determined by the spectrometric method [1].

2.3 Microbiological Analysis

For microbiological analysis, samples were collected in sterile glass dark bottles, which were transferred inside a portable refrigerator to the laboratory. Analysis of samples was made immediately after sampling. Samples collected 10cm below the water surface. Total coliforms (*TC*), faecal coliforms (*FC*), *Escherichia coli* (*E.Coli*), faecal streptococci (*FS*), and *enterococci* (*Ent*) were determined by the filtration method [1].

3. RESULTS AND DISCUSSION

The results of *in situ* measurements of the physicochemical parameters (T_{water}, *pH*, *DO*, *EC* and *TU*) for all sampling sites in each campaign are presented in Figure 2. T_{water} values in seawater ranged from 13.9 to 26.1°C and in other sites from 11.5 to 24.1°C. *pH* values in the seawater (Site A) were very stable (8.1 to 8.3), while in other sampling sites ranged from 6.8 to 7.9. *pH* levels at Patraikos Gulf were measured at a range from 8.1 to 8.3 [6]. In the seawater at the Rion-Antirrion Bridge area, T_{water} values from 12.8-24.0°C and *pH* values from 8.0 to 8.4 had been reported [7]. In the seawater of Piraeus and Perama Ports the corresponding values were 8.4 and 8.6, respectively [8].

TU values in seawater were (1.14 to 1.61 NTU) and in other sites ranged from 1.2 to 81.7 NTU. During the sampling periods infrastructure works were in progress. The levels of the seawater clarity were measured in the range 3.0 to 9.4 m. In the seawater at the Rion – Antirrion Bridge area the turbidity values ranged from 0.4 to 1.2 NTU and the water clarity values from 7.5 to 14.5 m [7].

DO values in seawater ranged from 5.1 to 7.5 mg/L, at Site B from 4.8 to 5.9 mg/L, in Glafkos River from 7.6 to 9.7 mg/L and in Diakoniaris River from 0.5 to 7.7 mg/L. *DO* values reported for Patraikos Gulf [6] ranged from 6.92 to 7.86 mg/L. At the Rion – Antirrion Bridge area, reported *DO* values range from 5.2 to 9.5 mg/L [7]. *DO* mean values of 9.7 and 10.0 mg/L were reported at Piraeus and Perama ports, respectively [8].

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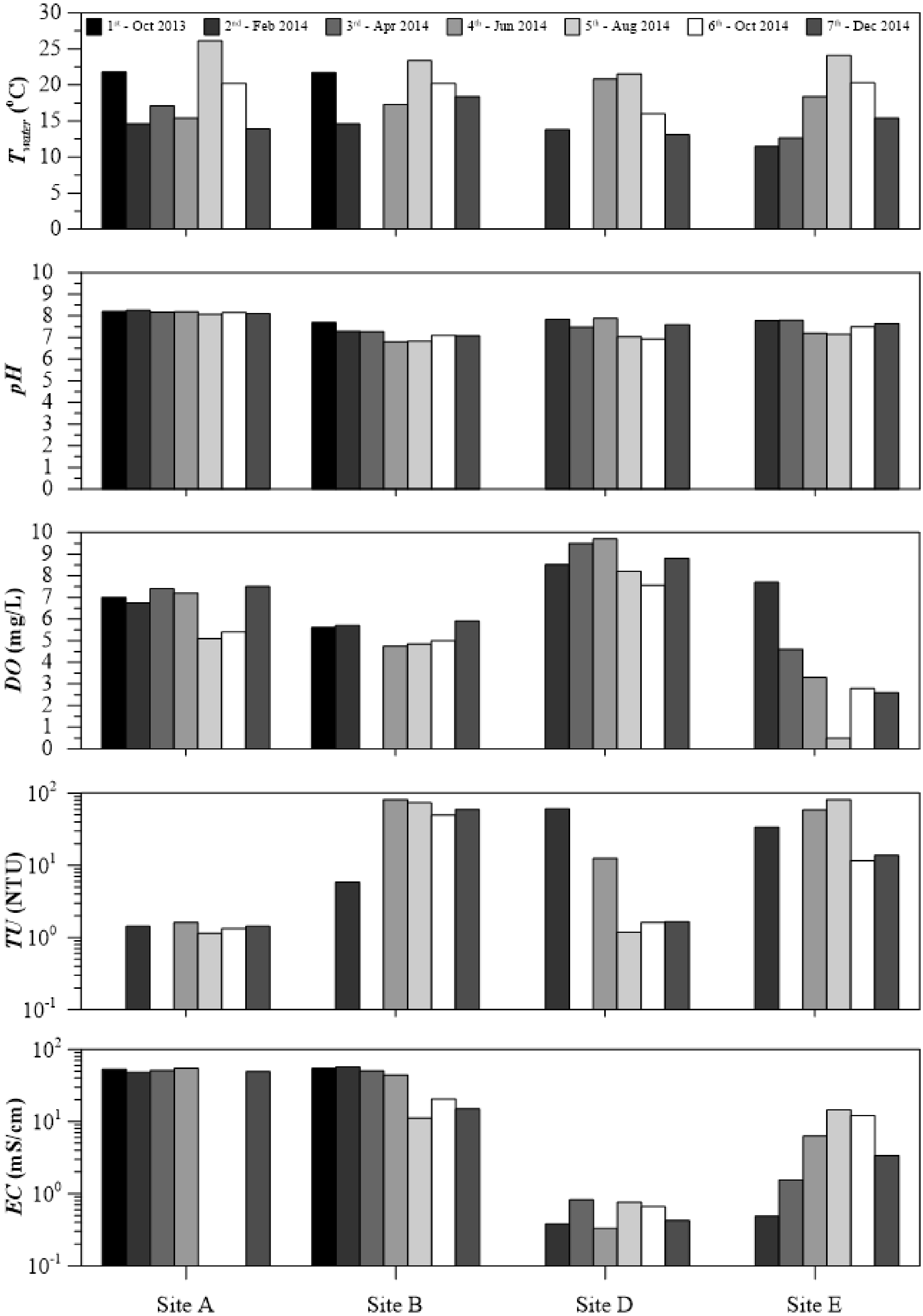


Figure 2. In situ measurements of water temperature (T_{water}), *pH*, turbidity (*TU*) and electrical conductivity (*EC*) at sampling sites at each campaign.

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EC values in seawater ranged from 48.3 to 54.4 mS/cm. At Rion – Antirrion Bridge area the *EC* values ranged from 56.4 to 58.7 mS/cm [7]. Mean values of *EC* were 43.2 and 43.8 mg/L at Piraeus and Perama ports, respectively [8]. *EC* values at Glafkos River ranged from 0.33 to 0.82 mS/cm. In the other sites intermediate values were measured due to interactions between sea and fresh water. Taking into account the values of T_{water} and *EC*, the saturation level (%) of *DO* in the seawater was calculated from 70.8 to 96.6% [5]. The corresponding values at the Ports of Piraeus and Perama were 126.0 and 126.4%, respectively [8].

The concentration of organic matter (BOD_5 and *TOC*), heavy metals (*Pb*, *Cu* and *As*), *Total-N*, *Total-P* and *Chlorophyll-a* at each campaign is presented in Table 2. BOD_5 values in seawater ranged from 0 to 0.5 mg/L, at Site B from 0.7 to 69.0 mg/L, in Glafkos River from 0 to 4.0 mg/L and in Diakoniaris River from 5.6 to 69.0 mg/L. At Patraikos Gulf the BOD_5 levels ranged from 5 to 20 mg/L [6]. At Rion – Antirrion Bridge area these values ranged from 0 to 0.7 mg/L [7]. *TOC* values in seawater ranged from <0.5 to 3.1 mg/L.

Total-N values in seawater were up to 1.5 mg/L, while quite higher values were observed in other sampling sites. *Chlorophyll-a* values in seawater ranged from 0 to 2.9 mg/L.

Pb concentrations were less than 10 μg/L at each sampling site during the whole sampling period. *Pb* concentration values at the Ports of Piraeus and Perama ranged from 72 to 360 μg/L [8]. *Cu* values ranged from ≤5 to 8 μg/L at Sites A, B and E while the corresponding values at Glafkos River were ranged from <5 to 18 μg/L. These concentrations were quite lower compared to *Cu* concentrations at the Ports of Piraeus and Perama (29 to 65 μg/L). Similarly, *As* ranged from ≤3 to 4 μg/L at Sites A, B and E, while the corresponding values at Glafkos River were ranged from 4 to 15 μg/L.

The concentration of the microbiological characteristics (Figure 3) was quite lower in seawater compared to those measured at the other sites. There is a significant variation of the concentration measured among the campaigns. At Site B, concentration values were similar to those of raw wastewater. In Glafkos River, concentration values were also similar to those of raw wastewater, and this implies discharge of wastewater from activities or houses installed across the river span. The concentration values in Diakoniaris River were similar to those of municipal wastewater without significant variation, indicating that the river was a constant source of microbiological pollution at the New Port of Patras.

4. CONCLUSIONS

The preliminary results of seawater quality measurements at the New South Port of Patras, Greece during the seven campaigns (October 2013, February 2014, April 2014, June 2014, August 2014, October 2014 and December 2014) and in comparison to older measurements at approximately the same location, and in other areas of Patraikos Gulf, as well as in other port areas in Greece, showed that the maritime area of the New Patras Port had satisfactory *DO* levels. The *pH* of seawater was in the same range of previously reported measurements in the major Patraikos Gulf area. Infrastructure work activities in the maritime and sea coast at the Patras New Port areas contributed to an increase of turbidity and decrease of water clarity levels. The *EC* values were about 12% lower than that measured previously in the Rion – Antirion Bridge area, which may be attributed to the inflow of freshwater from Glafkos R. and Diakoniaris R., which have significantly lower conductivity. The concentrations of *TC* and *FC* seem to vary widely in the maritime area of the New Patras Port, from < 100/100 mL to > 2000/100 mL, while the values of the parameters on the discharge points of Glafkos R. and Diakoniaris R. are higher, indicating that they are major microbial pollution sources of the marine area of the New Port.

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Table 2. Organic matter (*BOD*$_5$ and *TOC*), heavy metals (*Pb*, *Cu* and *As*), *Total-N*), *Total-P* and *Chlorophyll-a* concentration at sampling sites at each campaign.

Sampling Site	Campaign 1st	2nd	3rd	4th	5th	6th	7th
BOD$_5$ (mg/L)							
A	0.3	0.4	0.5	0	0.45	0	0.2
B	0.7	0.9	1.8	>4	>5	>2.5	69
D	4.0	2.6	0.3	0.85	0	0.9	3.7
E	*	>7.5	>5.6	>7	*	>7	69
TOC (mg/L)1.7							
A	<0.5	<0.5	1.5	2.4	3.1	1.5	1.7
B	<0.5	1.5	75.6	21	15.6	76	14.9
D	2	3	1.1	1.7	2.0	1.1	1.0
E	*	*	2.3	3.2	5.8	2.3	1.8
Pb (μg/L)							
A	*	*	<10	<10	<10	<10	<10
B	*	*	<10	<10	<10	<10	<10
D	<10	<10	<10	<10	<10	<10	<10
E	*	*	<10	<10	<10	<10	<10
Cu (μg/L)							
A	*	*	5	8	<5	<5	5
B	*	*	<5	8	<5	<5	<5
D	18	8	2	<5	<5	<5	8
E	*	*	<5	6	<5	<5	<5
As (μg/L)							
A	*	*	3	4	<3	<3	<3
B	*	*	<3	<3	<3	<3	<3
D	11	7	13	5	15	4	5
E	*	*	<3	<3	<3	<3	<3
Total-N (mg/L)							
A	<0.5	<0.5	1.5	<0.5	0.5	<0.5	<0.5
B	1.3	0.8	5.3	6.4	7.3	1.2	5.6
D	3.1	1.2	<0.5	1.2	3.3	20.5	14.3
E	*	3.1	<0.5	1.3	6.7	1.2	1.3
Total-P (mg/L)							
A	0.160	0.049	3.345	0.23	0.1	0.49	0.5
B	0.139	0.254	5.929	12.3	7.1	16.7	20.3
D	0.402	0.090	0.073	0.98	0.3	0.49	0.7
E	*	0.300	0.106	3.1	11.0	5.3	3.0
Chlorophyll-a (mg/L)							
A	0.40	0.001	0.00	1.10	1.81	0.56	2.9
B	4.00	0.00	0.00	3.20	0.73	1.87	1.79
D	0.00	0.001	0.01	0.50	10.0	10.8	4.4
E	*	0.00	0.03	0.10	1.15	1.57	1.72

(*) Sample was not collected.

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BOD_5 concentrations in the maritime area of the New Patras Port did not exhibit differences compared to the values that were measured previously in the seawater of the Rion – Antirion Bridge area, but were two orders of magnitude lower than those measured in the same area few years ago. Finally, the levels of heavy metals, *Pb*, *Cu* and *As*, were quite low, in both the sea area of the New Patras Port and Glafkos and Diakoniaris Rivers.

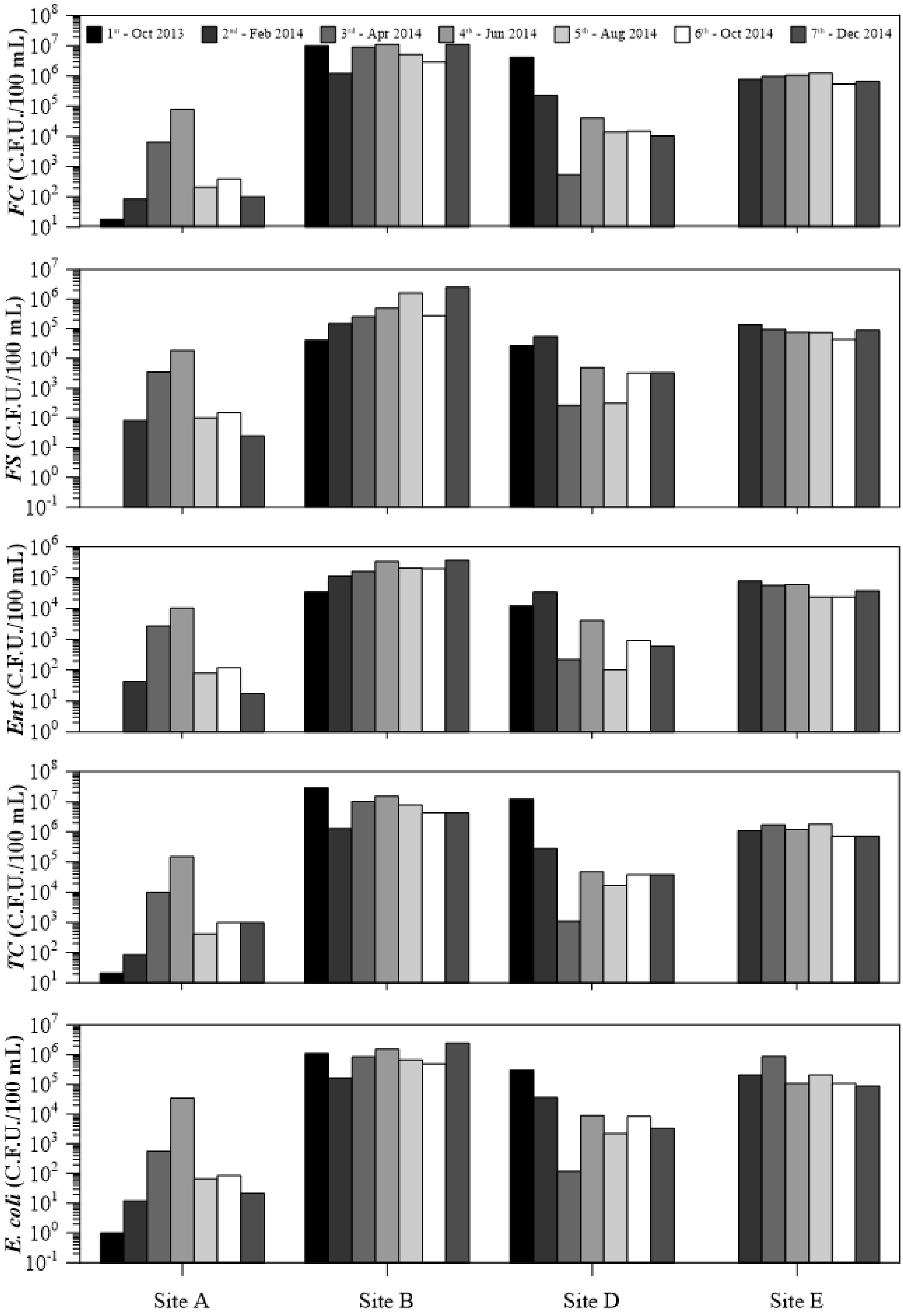


Figure 3. Water microbiological characteristics at sampling sites at each campaign.

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References

[1] APHA, AWWA, WEF, 1998. *Standard Methods for the Examination of Water and Wastewater*. 19th ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC

[2] Grasshoff K. *et al.* 1999. *Methods of Sea Water Analysis*. 1999 WILEY-VCH Verlag GmbH.

[3] Bloutsos A.A., Manariotis I.D. and Yannopoulos P.C., (2015). Concentrations of metals Pb, Mn, Fe in Alfeios river basin during the period 2006-2007. *Proceedings of the 3rd Common Congress – 13th Hellenic Hydrotechnic Society, 9th Hellenic Water Resources Management Committee and 1st Hellenic Water Link*. (eds. V.A.Tsixrintzis, K.L.Katsifarakis and G.P.Tsakiris) December 10-12, Athens, Greece, Vol.II, 689-696 (in Greek).

[4] ISO 7890-1:1986. Water Quality – Determination of nitrate – Part 1: 2,6 2,6-Dimethylphenol spectrometric method. International Organization for Standardization.

[5] http://water.usgs.gov/software/DOTABLES (accessed January 2015)

[6] Chalkidis D.A. and Tsolis A.K., 1982. Measurements of pollution parameters in Patraikos Gulf. Laboratory of Chemical Technology. University of Patras (in Greek).

[7] Antonopoulos I., Grigoropoulos S., Tsonis St. and Yannopoulos P., 1992. *Research on seawater physicochemical parameters and dynamic biological pollution at reef manufactures in Rion-Antirrion Area for the junction project*. Final report. Ministry of Environment and Energy – Department of Civil Enginnering, University of Patras, Greece (in Greek)

[8] Moustakis A.M., 2005. *Examination of Marine Pollution in the Coastal Area from Pireus to Perama*. PhD. Department of Maritime Studies. University of Pireus (in Greek).

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Assessing coastal zone response under extreme storm events for flood risk management. The case study of Rethymno, Greece

E. V. Kragiopoulou[1], E. S. Skarlatou[1], A. Lykou[2], C. Makropoulos[2], V. K. Tsoukala[1*]

[1] Laboratory of Harbour Works,Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou 5, 15780 Athens, Greece.
[2] Hydrology and Water Resources Utilization Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou 5, 15780 Athens, Greece.
*Corresponding author: Email: tsoukala@mail.ntua.gr

Abstract

Flooding has always been a serious problem for Rethymno, Greece as major flood events have been encountered throughout the years resulting in serious damages. For this reason, Rethymno city is one of the case study areas of PEARL project, an EU-funded research project, which aims to develop and apply adaptive risk management strategies for coastal communities against extreme hydro-meteorological events, minimizing social, economic and environmental impacts. Within this framework, estimating wave overtopping, wave run-up and coastal erosion in Rethymno is of great importance as consequences of coastal flood events arising from storms and storm surges, sea level rise and tsunami. In this study, XBeach numerical model is applied on the coastal zone of Rethymno in order to assess the coastal response to time-varying extreme storm events. The output obtained refers to hydrodynamics, sediment transport, bed update and wave run-up calculations, enabling the stakeholders to identify the most vulnerable areas.

Keywords: extreme storm events; flood management; hydrodynamics; sediment transport; wave run-up; XBeach; Rethymno

1. INTRODUCTION

Coastal floods are regarded as one of the most dangerous and harmful of all natural disasters.

Climate change combined with rapid urbanization and poor governance lead to a significant increase in the exposure of people, livelihoods, environmental services, resources and infrastructure of coastal communities to hazard.

Flooding has always been a serious problem for Rethymno, Crete, Greece. Major flood events have been encountered throughout the years, resulting in serious damages mainly in the Old Town of Rethymno and the east low-laying areas [1]. For this reason Rethymno city (Figure 1a) is one of the eleven case study areas of PEARL (Preparing for Extreme And Rare events in coastal regions) project, an EU funded research project, which aims at developing adaptive risk management strategies for coastal communities focusing on extreme hydro-meteorological events, with a multidisciplinary approach integrating social, environmental and technical research and innovation so as to increase the resilience of Coastal Regions all over the world.

Within this framework, the XBeach public-domain numerical model is used in this project. XBeach is a two-dimensional morphological model for wave propagation, long waves and mean flow, sediment transport and morphological changes of the near-shore area, beaches, dunes and backbarrier during storms [2].

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2. CASE STUDY AND STORM EVENTS

Rethymno city is sited at the Region of Crete in Greece (Figure 1a) and its population stands at 32,468 inhabitants (Census 2011) with a density of 140.12 population/km^2. As the 3rd most populous urban area in the island of Crete, commercial, administrative, cultural and tourist activities are being developed along the north coast where the city is located. The mean absolute altitude is 15 m [1]. The case study area includes the Port of Rethymno, located in the Northern area of Crete within the homonymous bay and the adjacent coastal area at the east (a total area of about 8 km^2,) with a coastline length of approximately 4 km (3760 m) and max depth equal to -23 m (Figure1b). The grid is constructed with dimensions 1500x5160 m in x- and y- axes respectively and the spatial steps are chosen dx=dy=5m. The wave run-up level is investigated in twelve cross-shore transects per 300m with the first one being located 100 m to the right of the port. The topography data were extracted from the Hellenic Cadastre map and the bathymetry data from the Hellenic Navy Hydrographic Service case study map. Figure 2a presents the initial bathymetry and topography of the case study area as shown in XBeach.



(a) (b)

Figure 1. (a) The location of the case study area in Greece, Crete (b) Grid dimensions, coastline, bathymetry contours and investigated profiles of the case study area

The coastal response is tested under four forecasting (period 2000-2100) storm scenarios (Table 1) obtained by SWAN model [8] for the mean wave direction i.e. for North, Northwest and Northeast wind directions. The frequency of each wave direction is shown in Figure 2b [8], where N wind is proved to be the most frequent and NE the less. The storm scenarios selected to be simulated by XBeach characterize the worst storm category of each wind direction and the results obtained concern the hydrodynamics and sediment transport calculations. Twelve profiles per 300 m as shown in Figure 1b are also investigated for each storm event in order to estimate the bed update and wave run-up level. Sediment properties are selected uniform sand with porosity of 0.4 and size of 0.2 mm.

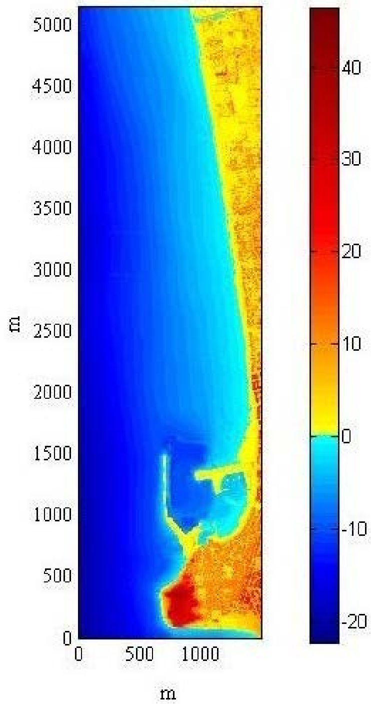
Table 1. Characteristic storm events simulated by XBeach

Scenario	Direction	Hs range (m)	Tp range (s)	Average Hs (m)	Average Tp (s)	Event Duration D (h)
1	N	2.01-4.61	6.71-9.28	2.86	7.85	103.5
2	N	2.46-4.95	7.84-9.65	4.18	9.07	72
3	NW	2.43-3.03	7.41-8.16	2.79	7.87	39
4	NE	2.07-2.66	6.78-8.96	2.41	8.16	24

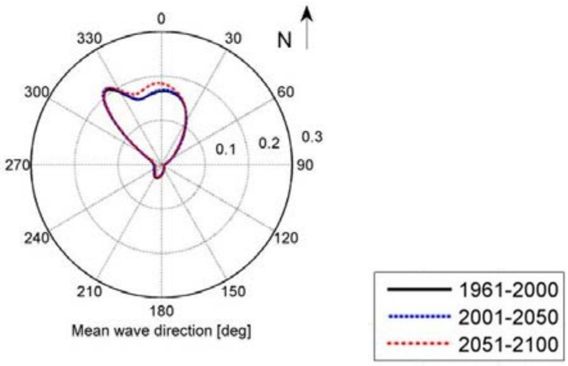
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3. MODEL APPLICATION

XBeach is a two-dimensional morphological model of near-shore processes to compute the natural coastal response during time varying storm and hurricane conditions including dune erosion, overwash and breaching. The model consists of non stationary shallow water equations, short wave propagation, sediment transport and bed update. In addition, a developed time-dependent wave action balance solver is included in the model to solve the wave refraction and to simulate the propagation and dissipation of the wave group [3]. To include short wave-induced mass fluxes and return flows in shallow water, the Generalized Lagrangian Mean (GLM) formulation is implemented. Additionally, the computational fluid dynamic is solved by Navier Stokes equations while the sediment transport rates are calculated using an advection-diffusion equation [4]. The numerical implementation is mainly first order upwind in line with the momentum-conserving form of Stelling and Duinmeijer method (2003), which improves long wave run-up and backwash on the beach [5].



(a)



(b)

Figure 2. (a) Initial bathymetry and topography as shown on XBeach (b) Mean wave direction at the case study for three time periods [8].

The XBeach model can be applied to areas extending several kilometers in the longshore and about a kilometer (several surf zone widths) in the cross-shore [4]. XBeach model has been shown to have quantitative skill in estimating storm impact, overwash and breaching processes on sandy beaches [6] like Rethymno's coastline. It is a public-domain model that has been developed with funding and support by the US Army Corps of Engineers, by a consortium of UNESCO-IHE, Deltares, Delft University of Technology and the University of Miami. More details about the model and its mathematical and theoretical background can be found at the user's manual [5,7]. XBeach is applied here in hydrostatic mode. Four different extreme forecasting storm scenarios (Table 1) obtained by SWAN model [8] for North, Northwest and Northeast wind directions (270°, 225° and 315° respectively, including ±45° incident wave directions) are simulated using the 2D

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instationary mode of XBeach based on a sequence of time-varying wave groups generated using a Jonswap spectrum (keyword: *wbctype=jons_table*). The results obtained are evaluations of wave height, velocities and sediment transport. Concerning the profiles for each storm event, they are investigated using the 1D transect mode for instationary conditions as well. The output refers to profile bed update, avalanching and run-up estimations. The wave run-up height is given by $R_{u2\%}$. It should be mentioned that the grid has been rotated counter clockwise at 90° so as the XBeach output could be directly comparable to MIKE21 results obtained in future projects.

4. RESULTS AND DISCUSSION

4.1 Hydrodynamics

The hydrodynamics calculations of the worst case scenario i.e. Scenario 2 (N-direction storm event with the highest identified significant wave height H_s=4.95 m and storm duration D=72 h), are presented in Figure 3. The output concerns the wave height H (m) and velocities u and v (m/s) on x- and y- axes respectively, referring to values at the cell centre. The computational x-axis is always oriented towards the coast, approximately perpendicular to the coastline while the y-axis is alongshore.

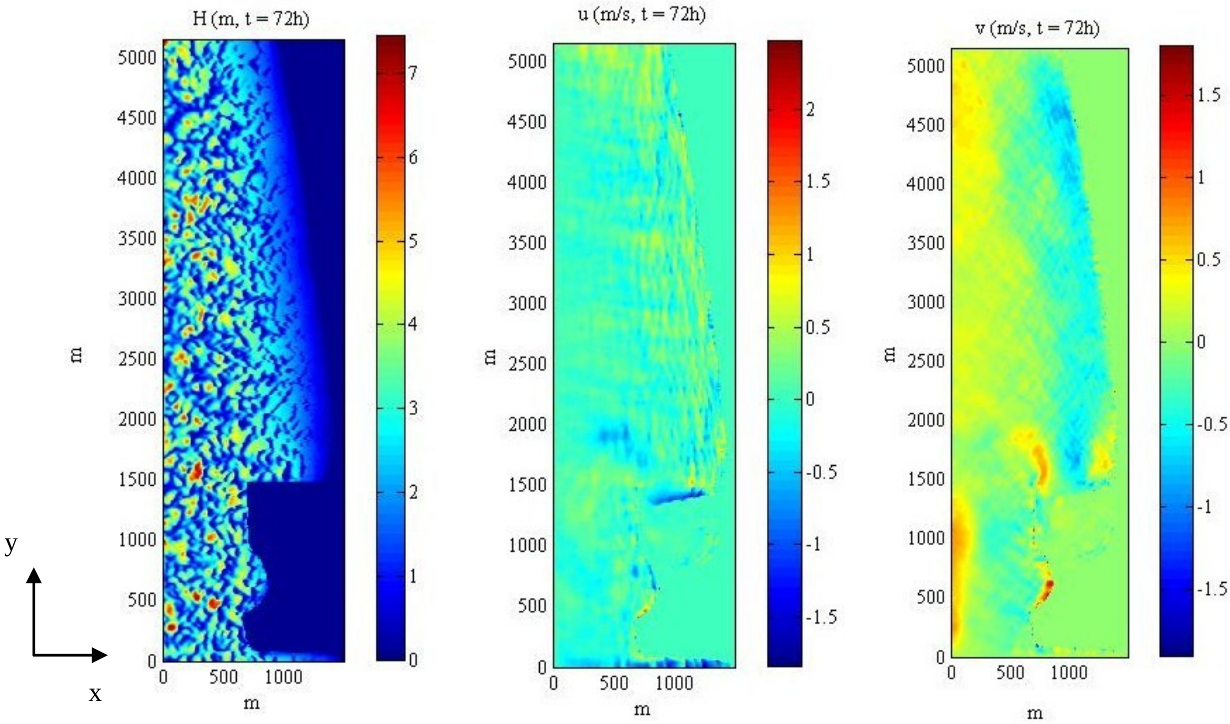


Figure 3. Spatial distribution of wave height (H) and velocities u, v (m/s) on x- and y- axes respectively for Scenario 2

4.2 Sediment transport

The output of the most important sediment transport occurring is described in Figure 4, i.e. for Scenario 2 and Scenario 4. In XBeach, the obtained results of sediment transport (m^2/s) are described in two dimensions (S_{utot} and S_{vtot} refering to x- and y- direction respectively) including both bed and suspended sediment transport, with the last one being the bulk of the total transport.

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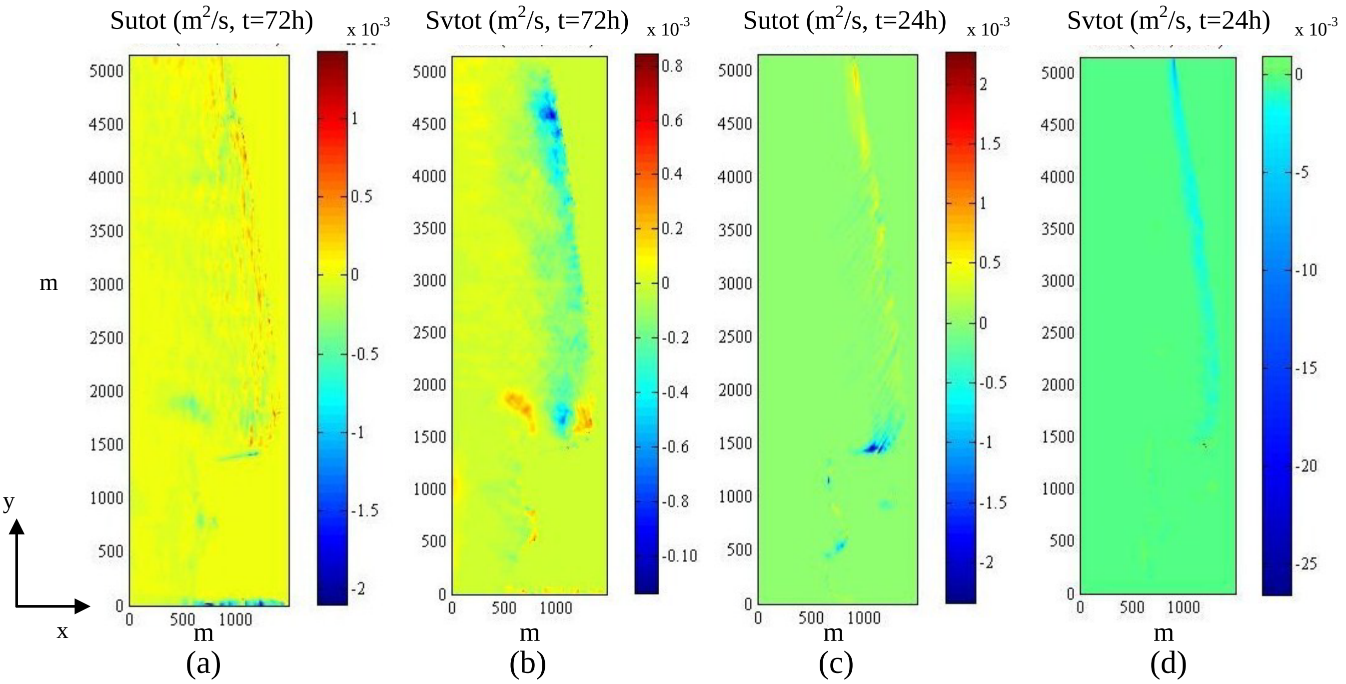


Figure 4. Spatial distribution of sediment transport for Scenario 2 for (a) x-axis and (b) y-axis respectively. Spatial distribution of sediment transport for Scenario 4 for (c) x-axis and (d) y-axis respectively.

4.3 Bed update and wave run-up

The bed evolution, dune erosion and wave run-up level of 12 different profiles were also investigated. As shown in Table 2, the profiles that proved to be the most vulnerable in common for all storm scenarios are transects no. 1, 6, 10, and 12 (Figure 1b) due to their high wave run-up level and/or the fact that a large distance of the inland area is flooding by the sea water. Profile no.12 bed update and avalanching results for all the investigated storm events are presented in Figure 7 as well as the time-varying evolution and flooding of Profile no.10 for storm Scenario 2 is depicted in Figure 8. Variable zs refers to the water level while zb refers to the bed level and zb0 to the initial bed level.

Table 2. Results of the most vulnerable profiles in common

	Storm scenario 1-N direction		Storm scenario 2-N direction	
Profile	**maxRu (m)**	**Inland distance flooding (m)**	**maxRu (m)**	**Inland distance flooding (m)**
1	1.1	125	2	140
6	1.2	40	2.3	45
10	1.6	35	1.8	115
12	2.1	35	2.3	50
	Storm scenario 3-NW direction		**Storm scenario 4-NE direction**	
Profile	**maxRu (m)**	**Inland distance flooding (m)**	**maxRu (m)**	**Inland distance flooding (m)**
1	0.9	15	3.5	160
6	0.8	30	2.3	60
10	0.7	25	2.8	165
12	0.8	25	4.2	145

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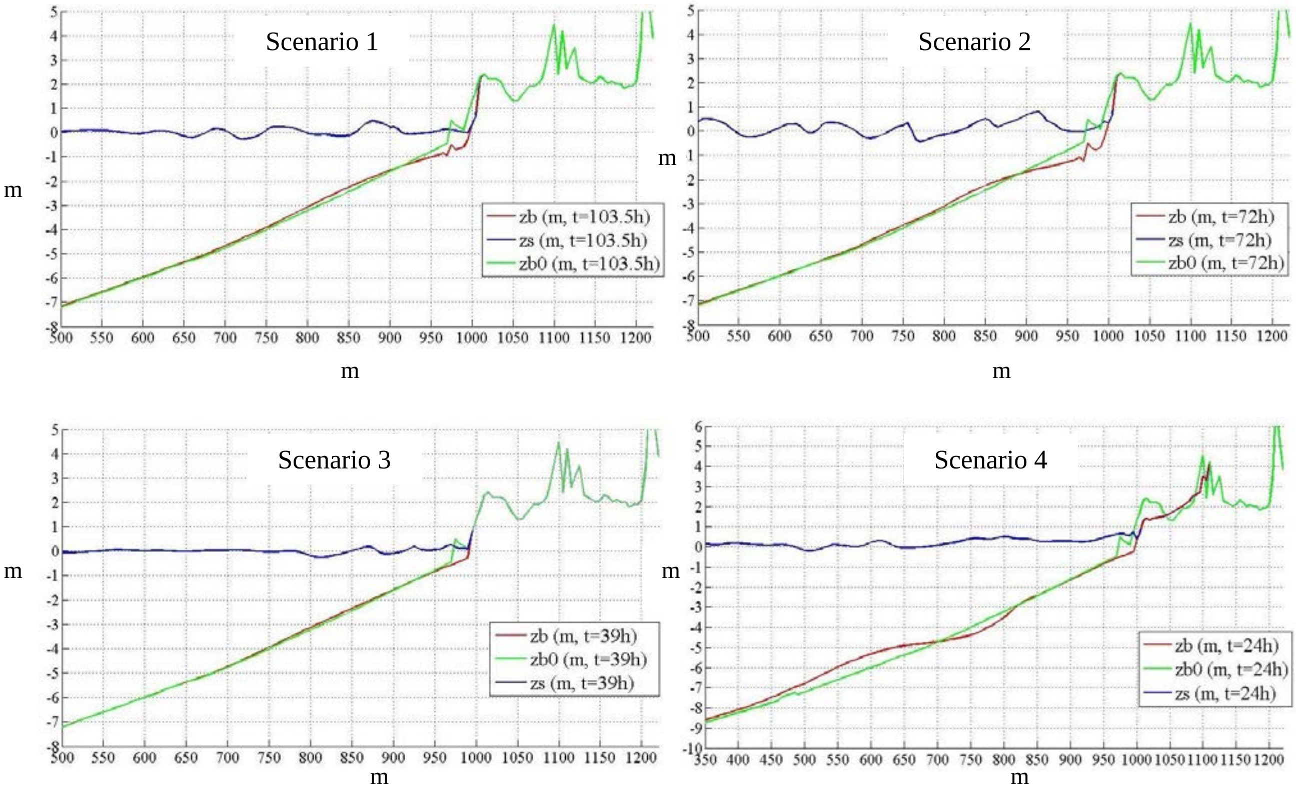


Figure 5. Profile no.12 bed update and avalanching at the end of each storm event

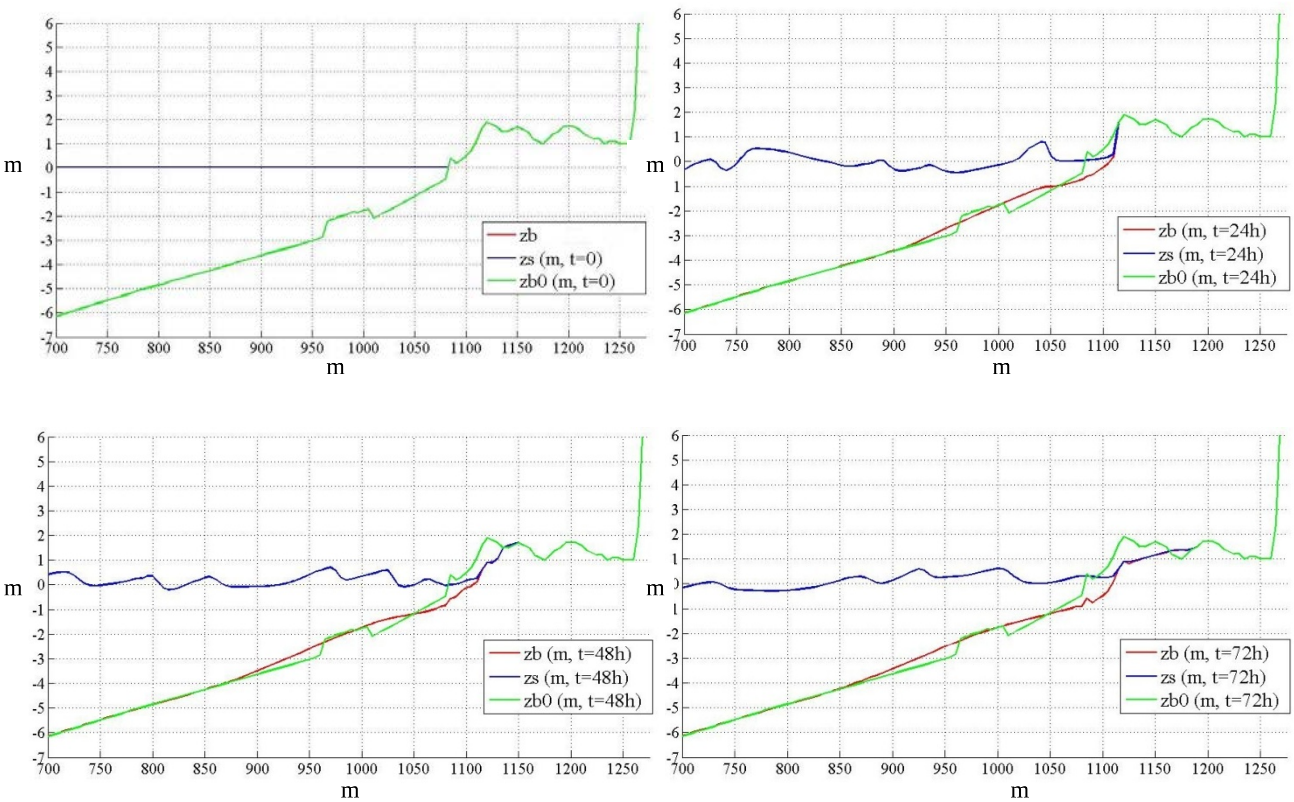


Figure 6. Profile no.10 time-varying evolution for storm Scenario 2

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5. CONCLUSIONS

The area is proved to be enough protected from NW direction storm events because of the Port presence, retaining low wave run-up heights all along the coast and no flooding problems are observed. The same though is not happening with N wind storms, which are also the most frequent [8]. In this case, wave run-up height ranges mainly between 1.5 and 2.5 m with the max values being observed both in the middle and in the end of the coastline, while flooding is occurring at the low-laying areas. The study area is also very sensitive to storms caused even by weak NE wind, where the wave run-up height gets up to 4.2m at Profile 12 and most of the profiles indicate flooding. As also shown in Figure 5, the severest bed evolution and dune erosion take place under NE storm events. Wave height can reach values up to 7 m in Scenario 2, while velocities are getting generally higher mainly around the port constructions and in the surf zone. Overall, the most vulnerable areas to erosion and flooding are the low-laying areas located at the east of the port and at the last 1 km of the study area, where the whole coastal area covered by sand and/or farmland is flooding. The narrow sandy area in the middle of the coastline is also vulnerable, as the sea water reaches the level of the street and the buildings both in Scenario 2 and 4. The fact that most of the profiles seem to be flooding usually during the first 3-6 hours of the storm event is also important. The cross-shore sediment transport is more intense for N wind storm events (max value 0.002 m^2/s), while alongshore sediment transport becomes more important for oblique waves (max value 0.005 m^2/s) indicating mainly beach erosion and not aggradation. The results obtained are very helpful for the stakeholders, as they play an important role to the development of an integrated flood risk management strategy focusing on the most vulnerable areas and the improvement of Rethymno's coastal area resilience against extreme and rare events.

Acknowledgements

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References

[1] Makropoulos et al. 2015, Managing flood risk in coastal cities through an integrated modeling framework supporting stakeholders' involvement: The case of Rethymno, Crete, *Proceedings of the 36th IAHR World Conference*, 28/6-3/7/2015, Hague, the Netherlands

[2] Roelvink, J.A, A. Reniers, A. van Dongeren, J. van Thiel de Vries, R. McCall , J. Lescinski. 2009. Modeling storm impacts on beaches, dunes and barrier islands, *Coastal Engineering*, **56**, 1133-1152

[3] Mehvar S., Dastgheib A., Roelvink J. 2015, Validation of XBeach model for wave run-up, *Proceedings of the 36th IAHR World Conference,* 28/6-3/7/2015, Hague, the Netherlands

[4] Bolle A., Mercelis P., Roelvink D., Haerens P., Trouw K.,2010, Application and validation of XBeach for three different field sites. *Proceedings of the International Conference on Coastal Engineering*; No 32 (2010): Shanghai, China, 2010

[5] Roelvink D. et al. 2010, XBeach model description and manual, Unesco-IHE Institute for Water Education, Deltares and Delft University of technology, report June 21 2010

[6] McCall R.T., 2008, *The longshore dimension in dune overwash modeling: development, verification and validation of XBeach*, MSc Thesis, Delft University of Technology

[7] XBeach Manual, Deltares, 2015 B, available on http://oss.deltares.nl/web/xbeach/ (accessed May 1st, 2016)

[8] Tsoukala V.K., Chondros M., Kapelonis Z., Martzikos N., Lyckou A., Belibassakis K., Makropoulos C.,2016, An integrated wave modeling framework for extreme and rare events for climate change in coastal areas-the case of Rethymno, Crete, *Oceanologia*, **58(2),** 71-89

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Protection and Restoration of Ecosystems

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

A qualitative method for mapping of pesticide loss risk in the area of Trifyllia in SW Peloponnese, Greece

T. C. Karyotis[1,2*], A. Ilias[1], P. Dalambakis[1], E. Hatzigiannakis[1], A. Tsitouras[2], S. Stathaki[1], J. Vrouchakis[1], K. Karyoti[1], G. Arampatzis[1], A. Panagopoulos[1]

[1] Hellenic Agricultural Organization "Demeter" - Soil and Water Resources Institute, Sindos, Greece
[2] Hellenic Agricultural Organization "Demeter" - Industrial and Forage Crops Institute, Larissa, Greece
*Corresponding author: Email: theodorekaryotis@gmail.com

Abstract

Pesticides are widely used by farmers in the Prefecture of Trifyllia, Western Peloponnese, Greece. In an attempt to understand the soil factors controlling losses of pesticides, surface soil samples were collected from 196 sites in the cultivated area of Trifyllia. Up to now, the pesticide leaching and runoff potential in the studied area is unknown. Soil organic matter (SOM) and textural classes were used and for practical reasons they grouped into four general classes. Based on SOM content and clay, the compiled map shows soil leaching potential (SLP) of pesticides in the cultivated areas of Trifyllia. According to soil texture, 3 moderate leaching risk classes, 2 high and 1 low were defined, and the respective classes based on SOM content were 3 low risk classes, 2 moderate and 1 class of high risk. Appropriate farming practices must be applied to decrease leaching or losses by runoff in order to minimise the pollution of shallow aquifers and surface waters in Southwestern Peloponnese.

Keywords: soil; pesticide; leaching; texture; organic matter

1. INTRODUCTION

In Greece, the pesticide pollution of the water resources varies and depends on climatic, soil and hydrological conditions which prevail in a specific agricultural area. The use of pesticides in agriculture often leads to groundwater pollution. It is documented that interaction of pesticides with soil, plays a dominant role in the extend of pollution. Knowledge of soil properties and evaluation of soil functions is essential for providing guidelines to support sustainable land management. Soil texture, soil organic matter, permeability, and soil structure [1,2,3,4] are among characteristics or properties which affect loss risk or retention into soils. Soil organic matter influences the quantity of water which is retained in the soil and the absorption capacity of pesticide. Increasing the soil organic content, such as by application of manure, the ability of soils is enhanced to hold both water and dissolved pesticides in the root zone.

Sorption of pesticides to soil is another process and is influenced by the physicochemical properties of the pesticide itself, as well as the properties of the soil. Correlations with pesticide solubility and sorption have also been reported [5]. Soil characteristics such as, organic carbon (OC) content, clay content, and pH are known to affect the immobilization and degradation of pesticides [6,5]. The incorporation of a pesticide into soil increases the availability for leaching. The rate and timing of a pesticide's application also are critical in determining potential of leaching. Leaching depends on the amount used, heavy rainfall or irrigation, and pesticides may be lost to groundwater. It is well known that site conditions affect the potential for leaching of pesticides and include: depth to groundwater, geologic conditions, topography, climate and irrigation practices.

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According to the European and national legislation regarding the plant protection products (European Directive 91/414, 1991) and the water safeguard, experience has been gained to assess groundwater vulnerability to pesticide at national or regional scale by using geo-information integrated with pesticide leaching models. An approach was developed [7] where the derived index is based on half-life of pesticide in soil and partition coefficient between soil organic carbon and water (K_{oc}). When half-life is longer, the length of time the pesticide remains in the soil is greater, hence the period for leaching is longer.

Leaching of pesticides to the groundwater is a subject of high importance for EU Countries because groundwater is the major source of drinking water and pressures from the application of pesticides in the intensively cultivated areas are very high. The leaching potential can be calculated with dynamic, multilayer, mechanistic models at different scales, including field, regional and national scale [1,8,9]. The EuroPEARL model was developed and indicators of pesticide leaching are included at the European level [10]. This model ignores losses by field drainage due to the lack of the respective information at European scale. A number of methods have been developed for assessing the leaching potential in soils with different characteristics. However, it is important to use a relatively simple approach that uses easily obtainable information to rank the pesticides losses based on basic soil properties.

This work deals with soil leaching potential (SLP) in the Prefecture of Trifyllia, Southwestern Peloponnese, where pesticides are widely used by farmers. For this aim, representative surface soil samples were collected from sites in the cultivated area, in order to map the soil loss potential of pesticides in the cultivated soils.

2. MATERIALS AND METHODS

Surface samples were selected from 0-30 cm depth for 196 sites in the area of Trifyllia, SW Peloponnese, from soils cultivated mainly with olive trees. Soil samples were taken after removing the fresh plant debris and three replicates per soil sample were conducted. These were air–dried and the fine fraction (<2mm) was used for laboratory analyses. Particle size distribution was determined by the Bouyoucos hydrometer method [11]. A modified wet digestion Walkley and Black method [12] was used for the organic matter determination.

Soil texture, organic mater content and slope are the parameters used for the pesticides risk losses. The classes and soil factors affecting groundwater pollution are presented in Table 1. The suggested soil textural classes include the following soil subclasses:

Class 1 (sandy): sandy, sandy loam, loamy sand
Class 2 (loamy): silty, silty loam, vf sandy loam, loam
Class 3 (clay loamy): sandy clay loam, clay loam, silty clay loam,
Class 4 (clay): sandy clay, silty clay, clay

Table 1. Soil factors included into the rating system for the assessment of leaching potential

Ranking	**Class 1**	**Class 2**	**Class 3**	**Class 4**
Soil texture	Sandy	Loamy	Clay Loamy	Clay
SLP	Very high	High	Moderate	Low
Ranking	**Class 1**	**Class 2**	**Class 3**	
Soil organic matter	<2%	2-3%	>3%	
SLP	High	Moderate	Low	
Ranking	**Class 1**	**Class 2**	**Class 3**	
Slope	0-2%	2-6%	>6%	
Runoff risk	Low	Moderate	High	

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The threshold value for soil organic matter (SOM) in agricultural soil is 2% by weight, beyond which soils cannot remain sustainable [13]. Taking into account this value, three soil organic matter classes were suggested (Table 1). In addition, textural and soil slope classes (Table 2) were used in this work, in order to calculate the losses potential. Slope classes of this system are in accordance to the Greek Soil Survey and these are for the classification of soil units.

It should be stressed that the above soil properties can easily be determined under laboratory conditions without difficulties or restrictions, while cost is not high and the required infrastructure exists in all soil laboratories dealing with soil analysis.

Table 2. Soil parameters and the suggested values for pesticide losses

SOM %	**SLP**	**Score**
<2	H	10
2-3	M	7
>3	L	4
Texture	**SLP**	**Score**
Loamy	H	10
Clay loam	M	7
Clay	L	4
Slope %	**Runoff Risk**	**Score**
0-2	L	4
2-6	M	7

Using SOM and soil texture, three indicative classes of soil leaching potential (SLP) are proposed : Low risk, value <10, Moderate 10- 15 and High with values >15. The respective values of pesticide losses which affect both leaching and runoff are: L<15, M 15-20, and H>20.

3. RESULTS AND DISCUSSION

The total study area consists of 32,016.1 ha, encompasses several municipalities and using the soil-landforms relationships, soil associations (Figure 1) were designated in the study area [14]. Field survey indicated that soils in the lowlands consist of alluvial deposits and the dominant parent material consists of conglomerates, hard limestone or marl. Most soils in the study area are characterized by alluvial and colluvial deposits; the cultivated soils occurring in this area are generally *Fluvisols*, *Cambisols* and *Luvisols* [15], while the non cultivated are very shallow with steep slopes and belong to soil association of *Leptosols* (Figure 1).

According to textural map (Figure 2) and Table 4, the majority of soils belongs to clay loamy textural class and covers 72.9 % of the cultivated area, while the loamy and clay soils cover 14.0% and 13.1%, respectively.

Soil organic matter can be readily transported off the field, and pesticides which are absorbed to SOM may also be moved with the eroded soil particles. A general slope map of Pelopennese was also compiled (Figure 3) and the cultivating area has a gradient less than 6% . More accurate map with two slope classes (0-2% and 2-6%) of the study area of Trifyllia are presented in Figure 5 indicating indirectly the potential vulnerable areas to runoff. Slopes promote fast surface runoff and reduced chances for water to infiltrate into the ground.

To reduce the runoff risk, farming practices such as strip cropping and buffer strips are suggested. In sloping areas, dissolved pesticides adsorbed to soil particles and can be moved across the agricultural soil by means of surface runoff. This is the most common pathway of pesticides from cultivated land as diffuse sources to surface water [16].

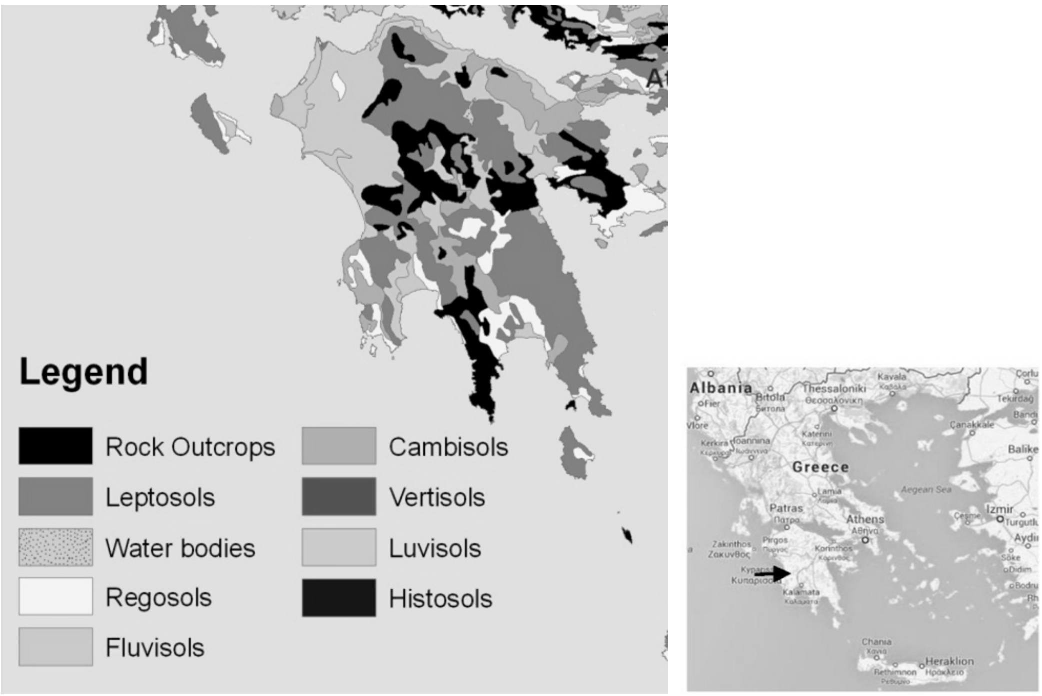


Figure 1. Soil association map of Peloponnese, Greece (Yassoglou 2005, as modified by Karyotis 2014)

Table 4. Distribution of soils after compilation of texture and SOM content

	Soil classes	**Texture**	**SOM %**	**Area (ha)**
1	SOMP_CL	Clay Loam	<2	886.4
2	SOMM_CL	Clay Loam	2-3	7,016.7
3	SOMM_L	Loam	2-3	3,926.6
4	SOMH_C	Clay	>3	4,176.1
5	SOMH_CL	Clay Loam	>3	15,439.7
6	SOMH_L	Loam	>3	570.6
			Total study area	**32,016.1 ha**

where: CL is clay loam, L** is loam and C***is clay texture*
SOMP is SOM<2%, SOMM is SOM 2-3% and SOMH is SOM >3%

It was estimated that pesticide losses in agricultural runoff have been quantified to assess the potential of contamination. It was estimated that they are typically less than 1.5% of the applied pesticide [17] and in some cases <0.1% [3]. It should be stressed that soils in Trifyllia (Figure 3) with slope >6% were recorded only in some very small spots and are not presented in the respective map (Figure 5), which depicts the classes of soil leaching potential.

Two dominant soil types of Tryfillia and the main characteristics are presented in Figure 4. These soils have different SOM content, depth, texture, degree of erosion and the surface horizons are acidic due to leaching of exchangeable bases.

By using the suggested values of parameters for the assessment of pesticide losses (Table 2), the soil leaching potential (SLP) for each soil class was calculated (Table 5). High SLP were observed in clay loamy soils with SOM<2% and in loamy soils with SOM 2-3%. Moderate SLP were recorded in clay loamy soils with SOM 2-3% or >3% and in loamy soils which contain SOM >3%. Low values have soils with clay texture and high content in SOM. In this class, pesticides can be absorbed significantly by soil organic matter. Also, most pesticides can be adsorbed to clay

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particles, become immobile, and leaching risk is reduced. This process minimizes the downward movement of pesticides, and reduces the possibility of groundwater contamination.

From Table 5, the areas with different degree of soil leaching potential were calculated and 71.9% of the cultivated land has moderate SLP, 15.0% has high and the rest 13.1% belongs to low SLP class.

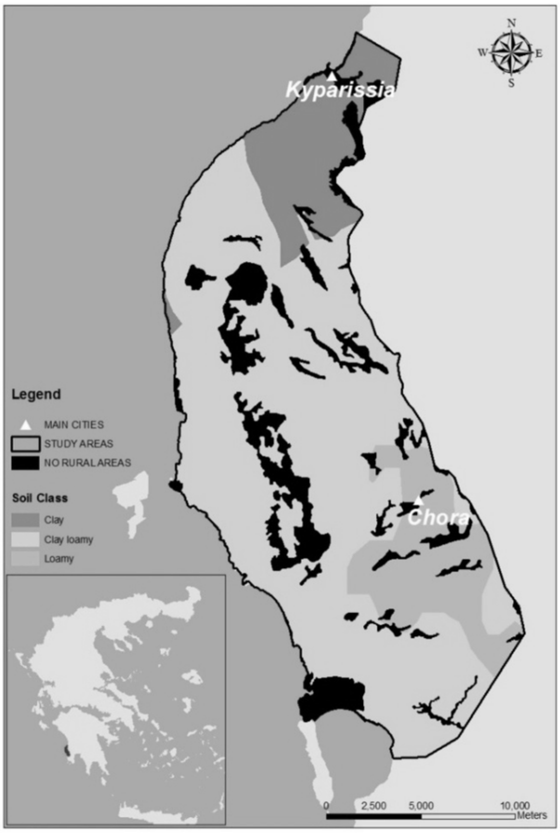


Figure 2. Soil textural map of the study area

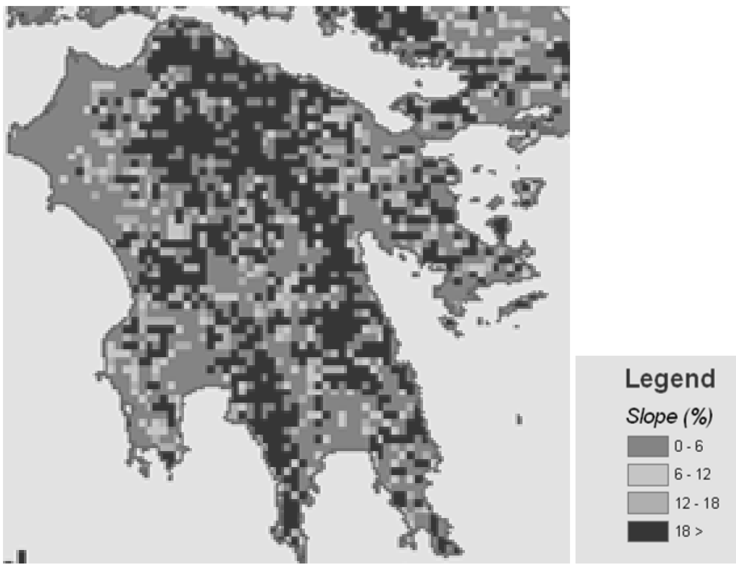


Figure 3. Soil slope map of Peloponnese, Greece

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Figure 4. Soils with SOM content > 2% in the surface horizons (left) and a strongly acidic soil with low SOM content (right)

Table 5. Soil leaching potential

Soil classes	SOM %	Texture	Ranking	SLP	Area (ha)
SOMP_CL	10	7	17	H	886.4
SOMM_CL	7	7	14	M	7,016.7
SOMM_L	7	10	17	H	3,926.6
SOMH_C	4	4	8	L	4,176.1
SOMH_CL	4	7	11	M	15,439.7
SOMH_L	4	10	14	M	570.6
				Total study area	**32,016.1**

Another attempt was made to assess the potential of pesticide leaching and runoff potential (SLRP), using SOM, texture and two slope classes. Results (Table 6) indicated that high SLRP was found in the following soil classes: clay loamy with SOM<2% and slope 0-6%, clay loamy with SOM 2-3% and slope 2-6%, loamy soils with SOM 2-3% or >3% and slope 0-6%. Apart from these soil characteristics, pesticide properties (solubility, adsorption), climate, farming practices (irrigation, cover crops, rotation schemes) quantity and frequent application of pesticides are among factors that also influence losses by leaching, runoff and adsorption.

Table 6. Soil leaching and runoff potential

SOM %	Risk	Score	Texture	Risk	Score	Slope %	Risk	Score	Total score	SLRP
<2%	H	10	CL	M	7	0-2 %	L	4	21	H
<2%	H	10	CL	M	7	2-6 %	M	7	24	H
2-3%	M	7	CL	M	7	0-2 %	L	4	18	M
2-3%	M	7	CL	M	7	2-6 %	M	7	21	H
2-3%	M	7	L	H	10	0-2 %	L	4	21	H
2-3%	M	7	L	H	10	2-6 %	M	7	24	H
>3%	L	4	C	L	4	0-2 %	L	4	12	L
>3%	L	4	C	L	4	2-6 %	M	7	15	L/M
>3%	L	4	CL	M	7	0-2 %	L	4	15	L/M
>3%	L	4	CL	M	7	2-6 %	M	7	18	M
>3%	L	4	L	H	10	0-2 %	L	4	18	M
>3%	L	4	L	H	10	2-6 %	M	7	21	H

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Figure 8, illustrates the leaching potential of pesticides for the wider area of Trifyllia in Southwestern Peloponnese. SOM remains the most important soil constituent influencing pesticide sorption in soils [4] even though clay content has an impact on pesticide sorption.

Organic matter and clay content together control the sorption potential of pesticides [18]. Soils with low sorption potentials are more sensitive to groundwater contamination than soils with high potentials. Interactions between leaching and sorption potential govern the overall sensitivity of the soil. A soil that has both a high leaching potential and a low sorption potential is the most sensitive, while soil with low leaching potential and high sorption is the least sensitive [18].

Fine textured soils rich in clay content have low sensitivities because they have slow permeability and high sorption potential. According to our rating system, soil leaching potential (SLP) is high in clay loamy soils with increased SOM and in loamy soils with moderate SOM content. Low SLP was observed in clay soils with low SOM.

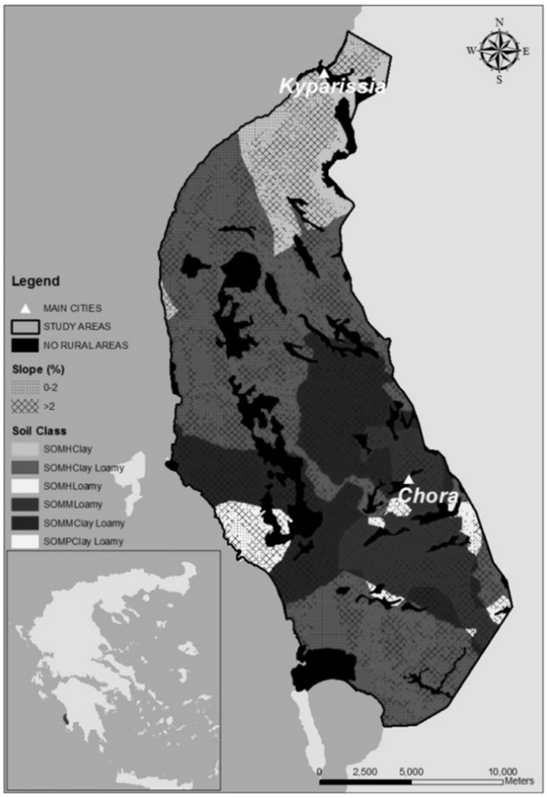


Figure 5. Soil leaching potential of pesticides for the wider area of Trifyllia, Greece

Appropriate farming practices must be applied to decrease leaching risk aiming to minimise the pollution of shallow aquifers in W. Peloponnese. This map can be used by local authorities in order to minimise potential negative environmental impacts of pesticide usage at farm level, and to suggest various mitigation strategies. Another potentially group of users are scientists working under the implementation of EU Water framework Directive in Greece.

4. CONCLUSIONS

Soil factors controlling losses of pesticides, and among them texture and SOM control pesticide movement in soil. Soil parameters were used and a practical and simple rating system was suggested for the soil leaching potential (SLP) for pesticides, in each soil class.

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A map was compiled regarding SLP for the wider area of Trifyllia in Southwestern Peloponnese. Leaching potential varied ammong soil classes and high risk is observed in clay loamy soils poor in SOM and in loamy soils of the area which have SOM content. This map illustrates low leaching potential in clay soils with high content in SOM . It has been calculated that 71.9% of the cultivated land has moderate SLP and 15.0% has high SLP.

Results have indicated that high LSP of pesticides (leaching and runoff) was found in soils with slope 2-6% and clay loamy or loamy texture. Losses in clay soils may be lower in comparison to the rest textural classes, and can be explained by the tendency of these soils to hold water and dissolved chemicals as they have more surface area on which pesticides can be adsorbed.

Drip irrigation is suggested as the most effective irrigation system and farmers have to use the lowest required volumes for rational irrigation, taking into account soil properties to minimize the pesticides leaching risk. However, to manage effectively the pesticide leaching, authorities, local agencies and land use planners have to deal with the identification of areas susceptible to pesticide leaching. Greece must prepare detailed SLP maps especially for the intensively cultivated areas by linking pesticide models with digital soil maps.

References

[1] Vancluster M., J. Boesten, M. Trevisan, C. Brown, E., Capri, O. Eklo, B. Gottesbüren, V. Gouy and A. van der Linden. 2000. A European test of pesticide-leaching models: Methodology and major recommendations. *Agric. Water Management*, 44:1-19

[2] Fogg P, Boxall AB, Walker A, Jukes A. 2004. Effect of different soil textures on leaching potential and degradation of pesticides in biobeds. J Agric Food Chem. 52(18):5643-52.

[3] Wu, Q., G. Riise, H., Mulder and L. Haugen. 2004. Influences of suspended particles on the runoff of pesticides from an agricultural field at Askim, SE-Norway. *Environmental Geochemistry and Health*, 26:295-302.

[4] Farenhorst, A. 2006. Importance of soil organic matter fraction in soil-landscape and regional assessment of pesticide sorption and leaching in soil. Soil Science Society of America Journal, Vol 70, pp. 1005-1012.

[5] Hiller, E., Krascsenits, Z., Cernanský, S., 2008. Sorption of acetochlor, atrazine, 2, 4-D, chlorotoluron, MCPA, and trifluralin in six soils from Slovakia. B. Environ. Contam. Tox. 80, 412-416.

[6] Barriuso, E., Feller, C., Calvet, R., Cerri, C., 1992. Sorption of atrazine, terbutryn and 2, 4-D herbicides in two brazilian oxisols. Geoderma 53, 155-167

[7] Gustafson D. 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry*, **Vol. 8**, pp. 339-357.

[8] Capri E., L. Padovani, and M. Trevisan. 2000. La previsione della contaminazione della acque sotterranee da prodotti fitosanitari. Quaderni di techniche di protezione ambientale. Pitagora, Bologna, Italy.

[9] Tiktat, A., D. de Nie, A. van der Linden and R. Kruijne. 2002b. Modelling the leaching and drainage of pesticides in the Netherlands: The GeoPEARL model. *Agronomie* 22:373-387

[10] Tiktak A, Boesten JJ, van der Linden AM, Vanclooster M. 2006. Mapping ground water vulnerability to pesticide leaching with a process-based metamodel of EuroPEARL. *J Environ Qual* **6**;35(4):1213-26.

[11] Gee, G. and J. Bauder. 1986. Particle Size Analysis. In *Methods of Soil Analyses*, Part 2, 2nd Ed.; Klute, A., Eds.; American Society of Agronomy and Soil Science Society of America: Madison, WI, 9: 383–411.

[12] Nelson, D. and L. Sommers, 1982. Total Carbon, Organic Carbon and Organic Matter. *In Methods of Soil Analysis*, Part 2; Book Series 9, Page, A.L., Eds.; American Society of Agronomy, Madison, WI, 539–579.

[13] Osman K.T. 2013. Forest Soils, Properties and management: Organic matter of forest soils. Springer, pp. 63-76, ISBN 978-3-319-02541-4

[14] Yassoglou, N. 2005. Soil association map of Greece. Edited by Agricultural University of Athens (in Greek)

[15] FAO/Unesco.1990. Soil map of the World. Rome, ISBN 92-5-103022-7

[16] Bach M., M. Letzel, U. Kaul, S. Forstner, G. Metzner, J. Klasmeier, S. Reichenberger and H. Frede. 2010. Measurement and modeling of bentazone in the river Main (Germany) originating from point and non-point sources. *Water Research* 44:3725-3733.

[17] Schottler, S.P., Elsenreich, S.J. and Capel, P.D. 1994. Atrazine, alachlor and Cyanazine in a large agricultural river system. *Environ. Sci. Technol.* **28**: 1079-1089.

[18] Huddleston, J.H. 1996. How soil properties affect groundwater vulnerability to pesticide contamination. Oregon State University

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Strategic sustainable development and ecotourism in natural ecosystems with archaeological heritage resources: The case of "Korikion Andron" Trail at the Parnassos National Park

T. Lanara[1], A. Mertzanis[2*], N. Tsaprounis[1], A. Mertzani[3], G. Varvarigos[1], E. Koukou[1], V. Margaritopoulou[1], T. Tsitsoni[1,4]

[1] Parnassos National Park Management Body, 35002, Amfiklia, Greece
[2] Technological Educational Institute of Sterea Hellas, Department of Forestry and Management of Natural Environment, 36100, Karpenisi, Greece
[3] National Technical University (NTUA), School of Electrical and Computer Engineering, Zografou Campus, Heroon Polytechniou 9, GR-15780, Zografou, Greece
[4] Aristotle University of Thessaloniki, Department of Forestry and Natural Environment, University Campus, 54124, Thessaloniki, Greece
*Corresponding author: Email: arismertzanis@gmail.com

Abstract

The mountain of Parnassos, crisscrossed by a dense network of trails, is one of the ten Mountainous National Parks of Greece (Parnassos National Park). Parnassos network of trails includes numerous hiking and mountaineering routes, with various thematic interests and degrees of difficulty, among which is the "Korikion Andron" trail, which is the subject of the present research. This trail, is of particular ecological, archaeological, geological and scientific research interest.

The main purposes of the present research are: a. the promotion of natural environment, biodiversity, landscape, geology, geomorphology, archaeology and mythology, b. the management and protection of the ecosystems and archaeological heritage resources and c. the strategic of sustainable development and ecotourism, in the wider area of the cave "Korikion Andron" at the Parnassos National Park. The appropriate signage and maintenance of the "Korikion Andron" trail, are prerequisites for the promotion and the safe use of the trail.

Keywords: ecotourism; sustainable development; natural ecosystems

1. INTRODUCTION

The mountain of Parnassos, crisscrossed by a dense network of hiking trails and mountaineering routes, is one of the ten Mountainous National Parks of Greece. Due to the modern lifestyle, trail walking and hiking offer unique opportunities for contact with nature, biodiversity, ecology and cultural heritage, ecotourism of each region [1].

In the past, most trails were opened to facilitate communication of mountain areas with the lowlands and larger towns, and between the villages. Many trails, especially those in rural areas, were also opened to serve the movement of people and animals, the local logistical needs and generally the agricultural and pastoral life of the residents. In modern times most of these trails are being used in different ways or have been abandoned altogether.

Nowadays, many of these trails, in the area of Mt Parnassos, have been mapped, upgraded and maintained under the responsibility of the relevant Forest Services, Parnassos National Park Management Body, Hellenic Federation of Mountaineering & Climbing, Hellenic Alpine Club of Arahova, and various groups of volunteers, leading to different degrees of alternation in their routes. In this way, they can be used both for outdoor recreation and for the promotion of

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environmental, archaeological heritage resources, traditional and mythological features. Certain trails have been marked with appropriate direction and description signs (trailhead information signs, information/interpretive signs, destination signs, reassurance markers/blazes, You-Are-Here signs, identification signs, etc.). An important factor to increase a trail's functionality and traffic is the proper (pre) design with specific technical specifications, to highlight its particular characteristics in tandem with the safe movement of visitors. This is also a factor to reduce maintenance costs and promote the rational management of a trail. Main tools to achieve this is the proper trail signage which makes visitors feel safe and comfortable, and the explanatory signs that promote public awareness [2].

In addition, the "ecotourism routes" in "Protected areas" and "Natural Parks" are among the most important "tools" that experts use in order to illustrate the environmental features, but also historical, archaeological data and culture of certain areas, such as the "Korikion Andron" trail at the Parnassos National Park.

2. MATERIALS AND METHODS

2.1 Geographical location of the study area

A dense network of trails are can be found at Mt Parnassos (Figure 1). "Korikion Andron" trail, the subject of this present research, is located in the south- eastern side of Mt Parnassos in Central Greece, in the prefecture of Fokida. Mt Parnassos, with Liakoura (2,456 m), Kalogiros (2,397 m), and Gerontovrachos (2,396 m) being the highest peaks, is one of most impressive and steep mountains of Roumeli (Central Greece). The main nearby villages are Eptalofos, Arachova, Delfi and Chrissa.

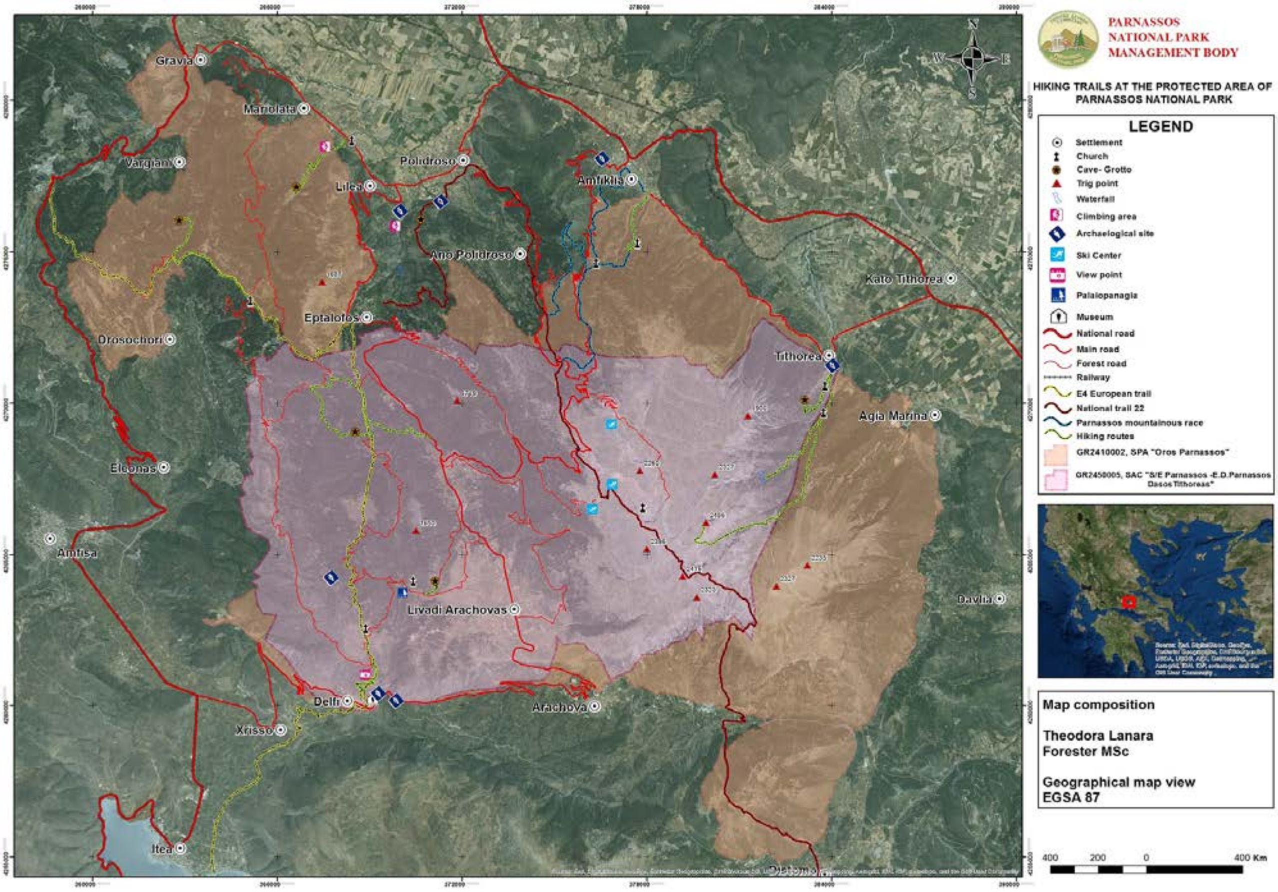


Figure 1: Map of hiking routes at the protected area of Parnassos National Park.

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“Korikion Andron” trail (Route I) starts from Palaiopanagia near Livadi Arachovas and ends after 1 hour to the Cave of “Korikion Andron” (Figure 2). From Palaiopanagia with South-South-West direction, a hiker can follow the route (Route II) that ends to archaeological site of Delphi, after of 3-3:30 hours of hiking, an alternative route having as starting point the archaeological site of Delphi through European trail E4 and at to the Cave of “Korikion Andron”. Southern Parnassos and especially “Korikion Andron” trail, is accessible to the visitor that comes from Athens via Livadia to Arachova village and then to Livadi Arachova. A trip from Athens to Arachova is 175 km long (around 1h 40m by car), while from Lamia to Livadi Arachova is 80 km long (around 1h 15min by car).

2.2 Investigation method

For the depiction of the environmental situation (vegetation, flora, fauna, geology, geomorphology, water resources, landscape), archeology and mythology, of Mt Parnassos and of the “Korikion Andron” trail, involved a series of different stages: the study of bibliographical references, systematic in situ observations (field-work), measurements using the Global Positioning System (GPS) satellite signals, observation and direct digitizing on the basis of different aged aerial photos and satellite images (Google Earth). Also, have been used topographical maps (Hellenic Military Geographical Service, scale 1:50.000 and 1:100.000), geological maps (Institute of Geology and Mineral Exploration, scale: 1:50.000), Digital Elevation Model (DEM) data (National Cadastre & Mapping Agency S.A.), hydrological data and forest maps of vegetation and land uses (Ministry of Reconstruction of Production, Environment & Energy, scale: 1:200.000). All primary data were imported in an apposite database and were transferred in topographical map and onto DEM data using ArcGIS for Desktop 10.3. Measurements were taken using the Trimble Juno 3D Series embedded with software ArcPAD 10.2.

2.3 Institutional frame of the region - Mt Parnassos Protection status

Mt Parnassos includes areas that are covered by a protection status at a National and Community level [3, 4]. These are more specifically the following: a. The Parnassos National Park, founded in 1938, for the protection of the mountain’s rich natural beauty. b. The Aesthetic Forest of Tithorea (200ha), for its special natural beauty and ecological importance. c. The Special Protection Area (SPA)-“Oros Parnassos” Code GR 2410002, for the protection of birds (NATURA 2000). d. The Special Area of Conservation (SAC)-“N.A. Parnassos-Ethnikos Drymos Parnassou-Dasos Tithoreas” Code GR 2450005, for the protection of types of habitats and species of flora and fauna (NATURA 2000) and e. The Parnassos National Park Management Body, founded in 2002, aiming mainly to the protection, conservation and sustainable management of the above mentioned protection areas and f. The Area of Outstanding Natural Beauty of Delphic landscape, for its aesthetic value and remains appreciably natural.

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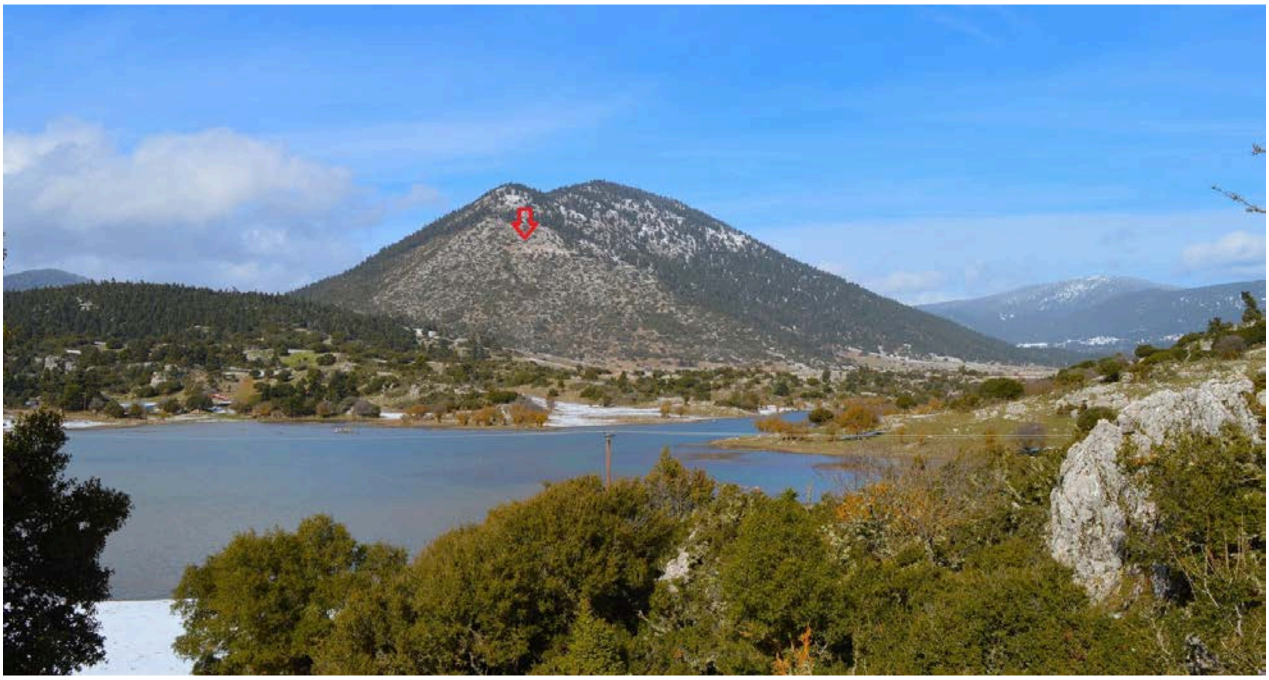


Figure 2. Palaiovouna Mt. (1,650 m) where “Korikion Andron” cave is located and the polje at Livadi Arachovas (Photo by Lanara T.).

2.4 Vegetation - Flora - Fauna

The vegetation zones encountered at the study area are: a. *Quercetalia pubescentis* (or deciduous broadleaf zone), consisting mostly of Quercus genus. forests. b. *Quercetalia ilicis*, consisting mostly of phrygana and maquis vegetation. The main plant species that occur in the study area are: kermes oak (*Quercus coccifera*), fir (*Abies cephalonica*), stinking juniper (*Juniperus foetidissima*) (Figure 3a), prickly cedar (*Juniperus oxycedrus*), jerusalim sage (*Phlomis fruticosa*), pink rock-rose (*Cistus creticus*), common hawthorn (*Crataegus monogyna*). At Palaiovouna area and the steep slopes of southern Parnassos Mt. above Delphi, a large number of rare and endangered plant species are found and are included in Annex II of Directive 92/43/EEC. Two endemic species of Parnassus are located in the area (*Centaurea musarum*, *Silene guicciardii*). The mountain of Parnassos is also important for the significant number and variety of protected aviauna species, particularly birds of prey. In Annex I of the Directive 2009/147/EC fifty five (55) birds (e.g. *Circaetus gallicus, Aquila chrysaetos, Bubo bubo, Dryocopus martius, Dendrocopos medius Dendrocopos leucotos, Sylvia rueppelli*) of the region are listed. As for other fauna species, thirteen (13) mammals (e.g. *Rhinolophus hipposideros*, *Rhinolophus ferrumequinum, Myotis myotis, Barbastella barbastellus, Dryomys nitedula)* six (6) amphibians (e.g. *Bombina variegata*, *Rana graeca*, *Triturus alpestris*), fourteen (14) reptiles (e.g. *Testudo marginata*, *Podarcis muralis*, *Lacerta viridis*) and ten (10) invertebrates (*Zerynthia polyxena*, *Parnassius mnemosyne*, *Parnassius apollo*, *Lucanus cervus*, *Grossuana delphica*, *Morimus funereus*), are listed in Annex II of the Directive 92/43/EEC. More common species such as the fox (*Vulpes vulpes*), weasel (*Mustela nivalis*), marten (*Martes foina*), wild boar (*Sus scrofa*) and wolf (*Canis lupus*) are also present at the area.

2.5 Geological setting - Geomorphology - Water resources

The morphology of the land relief, in the wider region of the Parnassos National Park, is defined by the mountainous massif of Parnassos with steep slopes, gorges and intense morphological contrasts. Mt Parnassos is the third highest mountain in Central Greece (Sterea Ellada), after the mountains Gkiona (Pyramida 2510 m) and Vardousia (Korakas 2495 m). The dominant structural elements are its limestone steep tops, with highest peaks Liakoura (2456 m), Kalogiros (2397 m), and

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Gerontovrachos (2396 m). The area near "Korikion Andron" cave is dominated by midslopes, while over Delphi large limestone precipitous slopes are encountered known as "Phaedriades", creating a compact and impressive natural wall which is a morphological discontinuity of several kilometers length [5]. From the "Phaedriades" gushes the Castalian spring which was very important for both the sanctuary of Apollo and the Oracle of Delphi (Figure 3b).




Figures 3a,b. Stinking juniper (*Juniperus foetidissima*) at "Kroki" area (Fig. 3a).
The twin rocks of the Phaedriades (Fig. 3b) (Photos by Lanara T.).

Due to the predominance of limestone (76.6%) on Mt Parnassos, karst phenomena are formed from its dissolution. As a result, Mt. Parnassos is mostly characterized by an underground drainage system and lack of surface flow, with sinkholes and caves, forming many karst springs at the foot of the mountain. Other karst formations are dolines and poljes [6]. Karst formations are an important element of the landscape and geomorphology of the region, such as the Eptastomos Sinkhole, the Karkaros of Lilaia, the polje of Livadi Arachova, Korikion Andro Cave (or else, Korykio Andro - Korikio Andro - Corycian Cave - Korykian Cave) and Neraidospilia Cave.




Figures 4a,b. The entrance of "Korikion Andron" cave (Fig. 4a).
The inside of "Korikion Andron" cave (Fig. 4b) (Photos by Lanara T.).

2.6 History and Archaeology

The trail leads to the famous Korikion Andron Cave (Figure 4a), which, according to Pausanias reports (Fokika) is "the most worth visiting of all the caves I saw"[7]. The Korikion Andro, sacred

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to the Corycian Nymphs and the Muses, and a place of worship for Pan, may be the first religious center and the first oracle of the wider area of Delphi. Excavations inside the cave report findings dating from the Neolithic (4th millennium BC) to the Roman period (2nd century BC.).

At the south foot of Mount Parnassos, set within a most spectacular landscape, lies the Pan-Hellenic Sanctuary of Delphi, with the most famous oracle of ancient Greece. Delphi was regarded as the center, or navel, of the world. Traces of settlements are rare and very fragmentary until the 8th century BC. That is when the cult of Apollo prevailed and so began the development of both the Sanctuary and Oracle. The first stone temples of Apollo and Athena were built towards the end of the seventh century BC. Between the sixth and fourth centuries BC, the Delphic oracle, which was regarded as the most trustworthy, was at its peak. It was delivered by the Pythia, the priestess, and interpreted by the priests of Apollo. Cities, rulers and ordinary people would consult the Olympian god expressing their gratitude with great gifts which gradually filled the Sanctuary [8]. The archaeological site of Delphi, due to the global historical value as aesthetic and artistic significance monument has been included in the World Heritage List of UNESCO. [9]

3. RESULTS AND DISCUSSION

3.1 "Korikion Andron" trail at the Mt Parnassos - The route

The suggested trail starts from "Paleopanagia", leading uphill on the eastern slope of "Palaiovouna" Peak (1650 m) to the Korikio Andro. The fastest way to get to the starting point is to follow the provincial road from Arachova to Eptalofos. After 8 km, on the left side of the road is a sign to the Korikio Cave at an altitude of 1120 m (Table 1). After about 20 minutes on the main forest road there is a sign suggesting the trail. It is signed with a triangular white and red frame, surrounded by scrub vegetation dominated by yew and semirocky ground, becoming rocky as we move uphill. After a 30 minute walk, a stunning view of the polje "Livadi" and "Gerontovrachos" (2396 m), the second highest peak of Parnassos Mt is being unfold. Climbing the carved stone steps a small plateau appears along with the small triangular entrance of the Korikio Andron Cave. Inside the highest height of the cave is 50 m and the length is approximately 100 m (Figure 4b). Stalactites and stalagmites compose impressive "sculptures". The cave was excavated in 1970-1971 by Pierre Amandry. The findings date back from the Neolithic to classical period, and mostly are painted pottery, figurines, jewelry, shells and animal bones had votive character [10].

From mentioned above plateau the panoramic view of the Corinthian Gulf and the mountains of the Peloponnese in the south, Kirfi Mt. in the southeast and "Livadi Arachovas" in the east is outstanding. The more adventurous hikers, after returning to "Paleopanagia" may head south - southwest on the forest road for 4000 m to meet E4 trail (Figure 5). After 800 m, following the trail-signs, the junction that leads to the worth visited view point "Kroki" is found. Continue on the E4 trail that leads to the archaeological site of Delphi (Figure 6a). The 3000 m zig zag trail is included in the Delphic landscape and coincides with the European trail E4.

Table 1. Main characteristics of "Korikion Andron" trail (Route I & II)

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	Route I (short trail): From Palaiopanagia, Livadi Arachovas, to "Korikion Andron"	**Route II** (long trail): From "Korikion Andron" to Delphi
Starting Point/Trailhead location:	Paleopanagia (Livadi Arachovas)	"Korikion Andron" cave
Trailhead elevation:	1,120 m	1,360 m
Finish- Korikion Adron cave (elevation):	1,360 m	----------
Finish- Delphi settlement (elevation):	----------	570 m
Minimum elevation:	1,120 m	570 m
Maximum elevation:	1,360 m	1,360 m
Altitude difference:	240 m	590 m
Route distance/Length:	1,000 m	10,000 m
Estimated Duration:	1:30 hour (including the return to the starting point)	3-3:30 hours (not including the return to the starting point)
Type:	Rocky trail (800 m), semi-rocky trail (200 m)	Semi - rocky trail (5,700 m), rocky trail (4,300 m)
Degree of difficulty:	Easy to Moderate	Medium to Moderate
Trail markings:	Good directional signs (red-white triangular frame)	Good directional signs (red - white square mark) and from Kroki to Delphi signs E4 trail (yellow - black - white square frame)
Vegetation:	Low bushes (*Quercus coccifera, Juniperus oxycedrus, Crataegus mongyna)* to the greatest sections, *Abies cephalonica*, *Juniperus foetidissima* in some parts	Low bushes to the greatest sections, dense fir forests (*Abies cephalonica*) in some parts, the clump of stinking juniper (*Juniperus foetidissima*) near "Kroki"
Points of interest/ Trail features:	Livadi Arachovas' polje, outstanding view, the beautiful chapel St. Triada surrounded by perennial kerme oaks, "Korikion Andron" cave, the entrance of cave: the panoramic view towards the gulf of Corinth, Kirfi Mt. and Gerodovrachos (2396 m), flora and fauna of Mt Parnassos.	The traditional settlement of Delphi and the archeological site, outstanding views, the wild beauty of the steep slopes, rocky cliffs "Phaedriades", wildflowers, "the landscape of Delphi": the panoramic view towards the gulf of Corinth, the settlements Itea – Crissa , Amfissa' Olive grove.
Recommended visitor season:	February to November	February to November

Source: Observations of the study group and various literature sources and existing reports.

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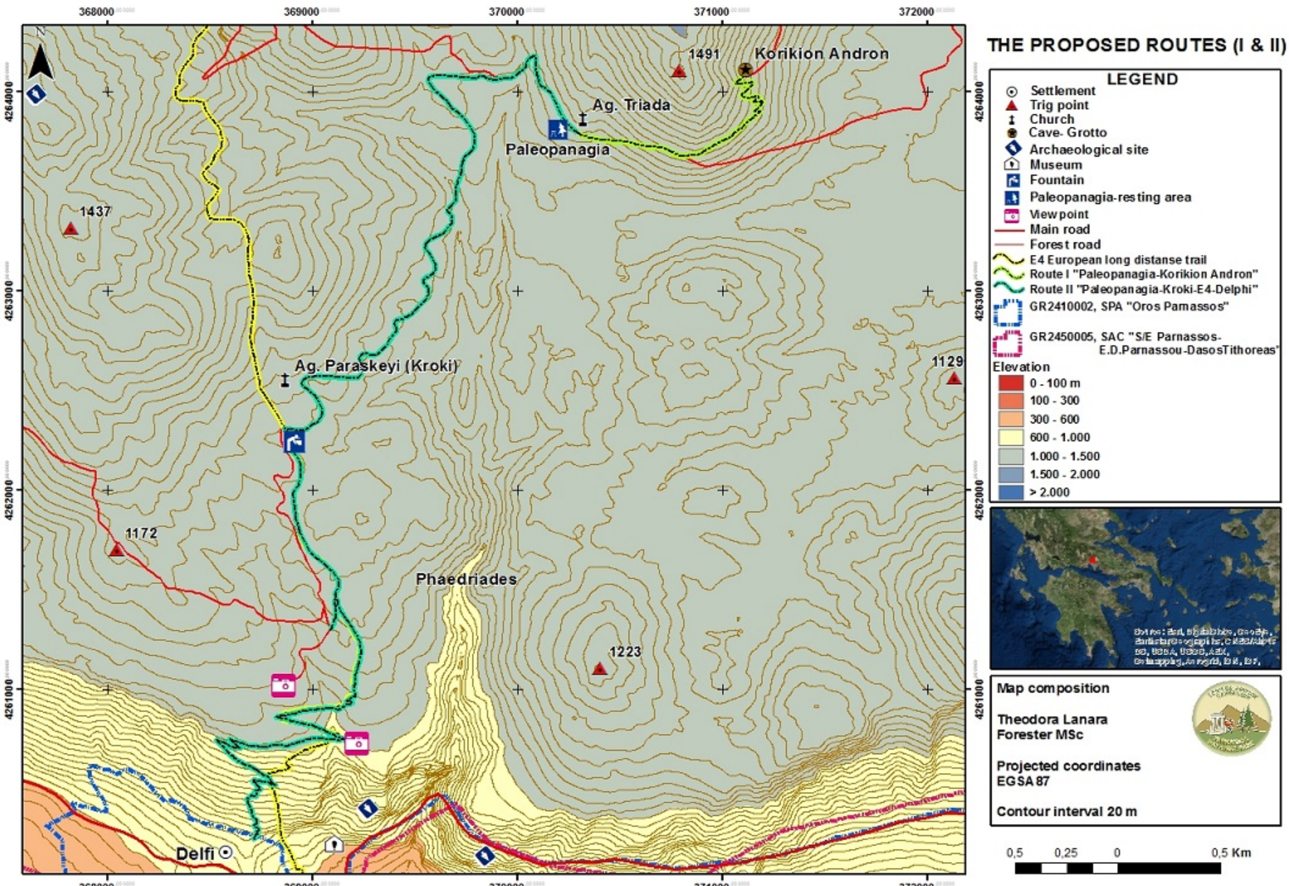
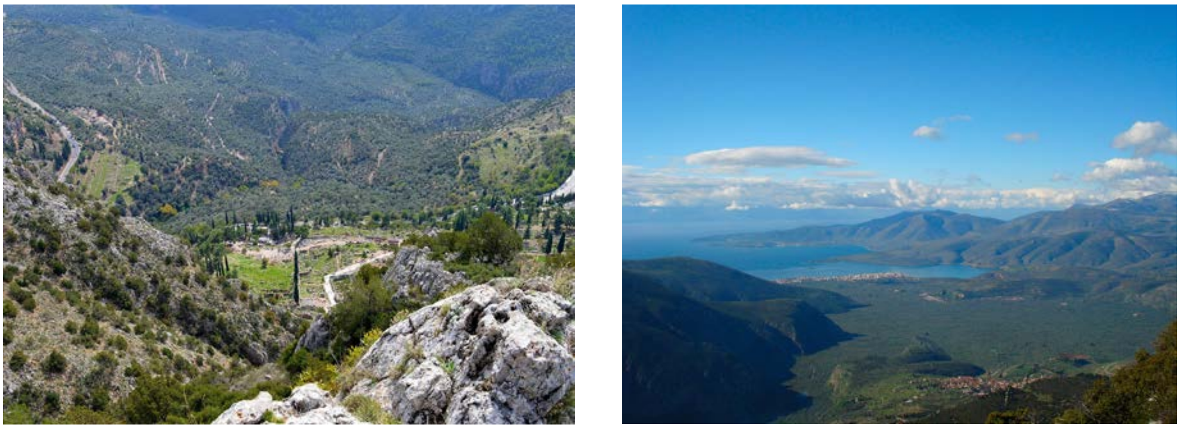


Figure 5. Map of the proposed routes (Route I &II) points of interest and points of view.

The view across the trial is stunning with the settlements of Delphi, Chrissa, Itea, Galaxidi and the Corinthian Gulf in the background. The archaeological site of Delphi, that has been included in the World Heritage List of UNESCO, appears in all its splendor.



Figures 6a,b. The archaeological site of Delphi from route II (Fig. 6a).
The Landscape of Delphi (Fig. 6b) (Photos by Lanara T.).

3.2 "The landscape of Delphi"

The "Delphic Landscape" is the wider area that includes the area of the archaeological site of Delphi, the traditional Olive Yard "Elaionas Amfissas" and the valley of the Pleistos River (Figure

6b). It has been declared as a protected area since 1981 and is consisted by two protection zones (A and B zone). Apart from the monuments of the archaeological site of Delphi, the Temple of Athena Pronaia, the Gymnasium and the Castalia Spring, the wider area of the valley includes numerous monuments and archaeological sites, from prehistoric to modern times, with special archaeological, historical, aesthetic value. The mentioned above, together with the natural environment that highlights the Delphic landscape, contributed to a cultural center of enduring value. The area is under special protection and management. Thus, only mild interventions are to be implemented aiming to the preservation and protection of the main features of the landscape.

3.3 "Korikion Andron" trail management – promotion and sustainable development

The preservation plan and some moderate customizations that have been suggested, aim to the conservation and protection of the paths' ecosystem, along with the cultural and archaeological heritage of the area. The plan is based on the fact that a well-structured path network will have minimal implications on the natural landscape, as well as on the path construction. Also, the technical specifications stated in the study aim to resource saving and in minimizing the future maintenance and management of the path (Table 2).

The thematic trails have turned into one of the basic forms of forest recreation serving ecological, educational, nature protection causes, while at the same time, someone can gain important information on the rich history of the area.

The identification, recording and evaluation of the problems that have been encountered as of now in "Korikion Andron" trail, are summarized in Table 2. This table serves as a tool for the trail manager, offering an overall mapping/visualization of problems and deficiencies. To facilitate the visualization and interpretation of the problems identified in the path, mainly related to the lack of constructions such as boardwalks and wooden steps, the insufficient signage, the proper maintenance (trail widening & clearing, tree & shrub trimming, etc.), one can find the geographical coordinates of the corresponding position below (Table 2). The appropriate signage and maintenance prerequisites for the safe use of the trail. According to N.C.N.S.T. (1996), signs are probably the quickest way to leave the trail user with a positive impression. The trail manager can transfer the relevant data (geographical coordinates) on a topographic map, or cartographic basis of his/her choice in order to use it in a more convenient way.

A complete management system aims to the utilization of an areas' specific characteristics: the views, natural and important historical sites, along with the development of forms of alternative recreation (ecotourism, geotourism, cultural-educational tourism) [9]. All the above will aid to the sustainable development of the area. Parnassos Mt is a living laboratory of nature and ecology with its important and sensitive ecosystems. The mountains' broader area could be a model of alternative forms of mountainous areas. The natural and cultural heritage of the region, is able to act as a development keystone and the local community can become the guarantor of its protection [12].

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Table 2. Inventory and Assessment of “Korikion Andron” trail (Route I).
Problems & proposals about the Trail Management

			Assessment of Trail Problems & Proposals about the Korikion Andron trail Management (Works Needed - Operations - Maintenance - Management)							
Geographical coordinates of the point / position	Place name	Point distance from the starting point of the trail (in meters)	-Trailhead information signs, kiosks or Information/Interpretive signs	-Destination signs, Reassurance markers/blazes	-You-Are-Here signs, Identification signs	-Route Improvement (Construction of Trail structures, boardwalks & wooden steps)	-Route Improvement (Trail widening & clearing, new improved route, tree & shrub trimming)	-Trail maintenance (User safety, access, protect adjacent resources, preserve trail investment, garbage, litter bins)	-Promotion & marketing (publicity), visitor monitoring & management	Remarks
370808,536 X 4263675,267 Y	Near Paleopanagia, starting point	0	●	●	●		●	●	●	1,2,3,4,5,6
371156,317 X 4263881,782 Y	--------	420		●				●		3,4,6
371175,550 X 4263925,842 Y	--------	520		●		●	●	●		3,4
371129,433 X 4263967,514 Y	--------	690		●		●	●	●		3,4
371093,185 X 4263974,209 Y	--------	725		●		●	●	●		3,4
383998,745 X 4270964,227 Y	--------	755		●		●	●	●		3,4
371144,229 X 4264040,496 Y	Panoramic view	820	●	●	●	●		●		3,4,5
371062,698 X 4264037,338 Y	--------	920		●		●	●	●		3,4,7
371071,588 X 4264048,239 Y	--------	940		●		●	●	●		3,4,6,7
371087,781 X 4264070,252 Y	--------	970		●	●	●		●		7
371114,081 X 4264106,871 Y	“Korikion Andron” Cave	1020	●	●	●	●	●	●	●	2,3,4,5,6
	Total length	1020								End of the trail (not including the return)

Source: Observations of the study group and various literature sources and existing reports Length.

Note: The dots (●) found at Table 2 indicate a problem/shortcoming in the infrastructure or maintenance of the corresponding point of the route. The dot also indicates that the management, promotion and marketing of the trail has been insufficient (or non-existent) and consequently there are measures that need to be taken both for the proper management and promotion of the trail but also for the protection and promotion of the natural environment of the area.

Remarks:

1: The starting point of the trail is near Palaiopanagia (Livadi Arachovas).

2: “Trailhead information sign/kiosk” or “Information/Interpretive sign”. The “Trailhead information sign” should include a double or triple bulletin board structure. The left display panel should contain general information about the trail (trail map/description). It should depict the general location of the trail in relation to other major landmarks [11]. “Information/Interpretive sign”, which should contain specific information about: a. Vegetation, flora & fauna of Mt Parnassos, b. Geoloogy – Geomorphology, c. Delphi’ landscape, d..Polje at Livadi Arachovas and e. “Korikion Andron” cave.

3: “Destination signs”, show direction and distances to various spots along the trail.
4: “Reassurance Markers”, are the paint or nail-on “blazes” that mark the trail. According to N.C.N.S.T. (1996), blazes should be within “line of sight” - when standing at a blaze marker, the hiker should be able to see the next one. Blazes should be continuous - even along road segments and other unmistakable parts of the trail. Blazes should be placed immediately beyond any trail junction or road crossing-even if there is a directional sign.
5: “You-Are-Here signs”, may supplement maps at trailhead kiosks and other key locations, such as at trail intersections, along the route [11].
6: “Identification signs”. They are simple, routed wood, identification signs which allow the hiker to find their location on a map in relation to what they are seeing. They are short and concise. Generally, an identification sign is appropriate for all sites listed on destination signs [11].
7: Reconstruction of the trail infrastructure or the construction of boardwalks & steps.

4. CONCLUSIONS

Parnassos network of trails includes numerous hiking and mountaineering routes, including thematic trails (nature trails, geological trails, trails, cultural heritage trails). The “Korikion Andron” trail is a combination of thematic trails, since it promotes the unique natural variability of the area, along with its geology, history and culture. The management and protection of the ecosystem and the archaeological heritage, the sustainable development and ecotourism in the area Parnassos Mt., is the main theme of the project. Any interference to the ancient trail that have been made in the past, is minimal and have been conducted by the Forest services. The future work that is proposed on project, based on sustainable development and promotion of the cultural/historical heritage is: a) Work aiming in the conservation and promotion of the paths’ unique characteristics, b) Trail-blazing, c) Improvement of the trail and d) Promotion of the unique identity of the place and its history (ecological awareness, cultural heritage, ecotourism, suggested future trails).

References

[1] M.A.R.D. & E-Department of Forests. 2011. *Guide to create and management of forest trails in Cyprus*. Ministry of Agriculture, Rural Development and Environment, Nicosia, Cyprus. pp. 37.
[2] Siafali E., Karagianis E., 2015. Technical provisions of trails at mountainous forests and woodlands. *Proceedings of the 17th Hellenic Forestry Conference “The contribution of modern forestry and protected areas in the sustainable development”*, 4-7 October, Cephalonia island, Greece. 613 – 624.
[3] M.E.P.P.P.W.-Ministry of Environment, Physical Planning and Public Works. 2003. *Special Environmental Study for Parnassos National Park*. Environmental Planning Department, Natural Environment Management Division. Athens.
[4] Dimopoulos, P., Bergmeier, E., Theodoropoulos, K., Fischer, P. and Tsiafouli, M. 2005. *Monitoring guide for habitat types and plant species in the Natura 2000 sites of Greece with Management Institutions*. University of Ioannina and Hellenic Ministry for the Environment, Physical Planning & Public Works. Agrinio, Greece. 172p.
[5] Lekkas E., Gouliotis L., 2010. *Delphi: a unique monument at an active geodynamic environment*. Training course, Seismic Risk Assessment in Specific Areas with Monumental structures. Earthquake Planning & Protection Organization, 6-10 December, Athens, Greece.
[6] Monopolis D., 1971. *Hydrological study in the karstic region of Parnassos mountainous complex*. Study No 4. I.G.M.E. Athens.
[7] Papaxatzis N., 1992. *Description of Greece, Pausanias.* Ekdotike Athenon, Athens
[8] http://odysseus.culture.gr (accessed February 15th, 2016)
[9] Tsaroucha A., 2012. *Cultural routes in a world heritage site, Delphi*. 4th Archaeological meeting of Thessaly and Central Greece, From Prehistory to contemporary Period. 15-18 March, Volos, Greece.
[10] Ecole Francaise D’ Athenes, 1981. L’ Antre Corycien I. Bulletin De Correspondance Hellenique (BCH), supplement VII, numero 1, 3-28.
[11] N.C.N.S.T.-North Country National Scenic Trail. 1996. *A handbook for trail design, construction, and maintenance*. U.S. Department of the Interior-National Park Service, pp. 342.
[12] Tsitsoni T., 2014. *Parnassos natural and cultural monument-Development keystone of the area*. Interdisciplinary workshop “Environment and Culture, Yesterday and Today”, 29-30 March, Lamia, Greece.

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Bio-security risk assessment of ship discharged ballast water based on some underlying theories

I.K.E. Ekweozor[1*], L. A. Kuroshi[2], O. Linden[2]

[1] Department of Marine Biology, Rivers State University of Science and Technology, Port Harcourt, Nigeria
[2] World Maritime University, Fiskehamnsgatan 1, P. O. Box 500, SE 201 24 Malmo, Sweden
*Corresponding author: Email: iekweozor@hotmail.com

Abstract

The arrival of exotic marine species in a new area increases with proximity to seaports, thereby raising seaports bio-security concerns. The objective of this study is to show theoretically, how the paradigms of 'spatial sorting', 'Swiss cheese model' and ' tens rule' could be used to determine the invasion potentials of planktonic species introduced into a harbour via Ships' ballast water. Based on the ballast water samples collected, the probability (at *a priori* α-level of 0.05) of species found in sampled ships becoming invasive is not significant at $p=0.043$. The resultant propagule pressure could be sufficient to satisfy the requirements of regulation D-2 of the Ballast Water Management Convention (BWMC) of International Maritime Organization (IMO).

Keywords: ballast water management; Harmful Aquatic Organisms and Pathogens (HAOP); Swiss cheese model; Spatial Sorting; Tens rule

1. INTRODUCTION

Shipping is the heart of International trade as most of the world's trade depends on shipping. Shipping moves over 90% of the world's commodities. In the bid to move these cargos, ships tend to transfer approximately 10 billion tons of water known as ballast water internationally each year and an estimated 7,000 marine and coastal species are stowed away daily in the process [1] to new climes. The cargo and the ballast water singularly or in combination provide a safe immersion level for propulsion and maneuverability for the ship. Ballast water is therefore, the water used by ships to achieve a correct immersion level and to maintain balance after cargo is discharged.
Studies by Gollasch and Leppakoski [2] for example showed that the survival rates of organisms within the ballast water tank decreases with time. With the advent of faster and bigger ships, the probability of this transfer has increased tremendously because of the reduction in voyage duration and the increase in the quantity of the organisms within a much bigger ballast water tank. A typical ballast water tank in a ship could take an amount of water that can be between 30-50% of the overall weight of the ship. That's an enormous quantity of water representing between 13 to 32 thousand metric tons of water, depending on the size of the ship [3].

1.1 Bio-security risks of ballast water

The arrival of marine exotic species in a new area increases with proximity to seaports. This is as a consequence of the ballasting and deballasting activities of ships on international voyage at the seaports (Figure 1). Invasions in seaports therefore, are unintended and unavoidable externalities of shipping trade. These therefore have defined the seaports as high-risk nodes [1] or invasion fronts [4]. A study was able to show that the annual-displacement of pioneer invaders is twice as far compared with post-colonization conspecifics [4]. This makes protecting national borders against possible biological invasions a very difficult undertaking.

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Marine exotic species or Harmful Aquatic Organisms and Pathogens (HAOP) can completely alter aquatic systems by displacing native species, degrading water quality, altering trophic dynamics, and restricting beneficial uses [5]. The potential of species transfer is compounded by the fact that all marine species have planktonic stages in their life cycle, which may be small enough to pass through a ship's ballast water intake ports and pumps. These include bacteria and other microbes, small invertebrates and the eggs, cysts and larvae of various species.

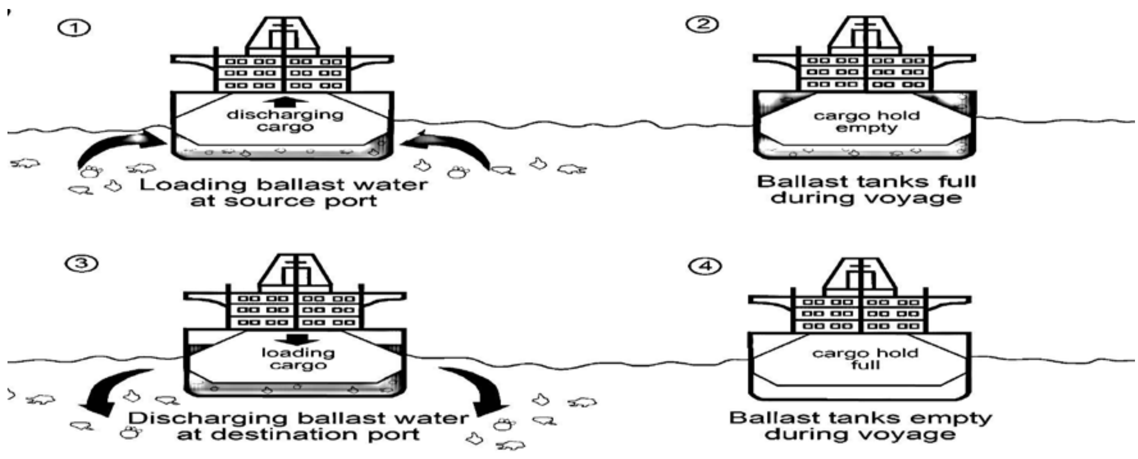


Figure 1. Uptake and discharge of marine species via ship's ballast water in seaports [3].

Even species in which the adults are unlikely to be taken on in ballast water, because they are too large or live attached to the seabed, may be transferred in ballast during their planktonic phase [6].

1.2 Invasion pathway

In the context of this study, the invasion pathway between donor and recipient ports is lined with a battery of environmental hurdles for HAOPs to surmount in the form of predators, temperature, salinity, water flow variance etc. This is however circumvented when the organisms utilize the most commonly available anthropogenic transfer mechanism (i.e. transport vector) provided by international shipping in the ports. Once they are able to survive the prevailing harsh conditions within the ship's ballast tank, they are successfully hitchhiked to a new environment. Studies have shown that over 90% of organisms in the ballast water tank do not survive a voyage [7; 8; 9; 10]. As soon as they are discharged into the new environment, their fate will now depend on the availability of suitable abiotic conditions (such as temperature and salinity) and friendly biotic conditions (such as presence of prey, absence of predators, competition, disease and parasites). These new arrivals are also expected to be in sufficient numbers (otherwise refer to as propagule pressure) to survive, spread, be established and ultimately become invasive within the new habitat.

1.3 Problem statement

As a consequence of the essential economic activities of shipping, the likely ecological and economic impact that may result from the discharge of planktons found in ships ballast water transported from one port environment to another, especially when they transform into marine pests, informs the necessity by this study to show how the underlying principles of some theoretical concepts can be applied in determining the bio-security of coastal seaports.

Measures to manage the bio-security risks of ballast water can be either onshore or shipboard. Onshore measures entail either managing the risk before voyage or after voyage. While shipboard measures entail either exchanging species rich coastal ballast water with species deficient mid-ocean water via a ship-safety procedure known as ballast water exchange (BWE) or treating the ballast water via treatment systems installed onboard the ship. The International Maritime Organization (IMO) through the ballast water management convention (BWMC), 2004 [11], has stipulated some prescriptive measures to mitigate these risks associated with ship-borne transfer of HAOPS in ballast water. These measures are in the form of numerical discharge standards for organisms known as performance standards (regulations D-1 and D-2).

2. SOME UNDERLYING THEORIES

An understanding of some underlying dynamics of invasion is critical to invasion management and control. The most documented data on invasion for example is the cane toad's colonization of Australia. A better understanding of the invasion dynamics can be achieved according to Urban *et al*. [12] by considering the multi-spatial dimension of invasion as well as the effect of environmental heterogeneity and the dynamics of evolution. The effect of introduced species population density and natural occurring and anthropogenic barriers placed on their pathways to invasion are also critical.

2.1 Spatial sorting

Charles Darwin in his 1859 work proposed the natural selection mechanism where organisms are differentially successful over time. In modern seaports however, there is a different predominating reproductive success concept. That is the concept of spatial sorting, where organisms are differentially successful through space rather than through time. This concept describes the assortative manner by which population mate at spreading vanguards or invasion fronts [13] like the seaports. At the invasion front (e.g seaport), heritable variation could lead to some phenotypic attributive evolution. This ultimately will result in the phenomenon of spatial filtering [4] where fast-dispersing individuals will mate with only their kind (fast-dispersing counterparts) producing even much more dispersive offspring with more sophisticated dispersal-enhancing mechanisms than their forebears [4]. This explains why seaports are critical invasion fronts.

2.2 Swiss cheese model

The Swiss cheese model (SCM) proposed by Reason [14] used Swiss cheese as a metaphor for barriers that could be used to prevent accidents from occurring (Figure 2). It likens human-induced safety systems to multiple slices of Swiss cheese, stacked side by side. It is an accident risk reduction strategy.

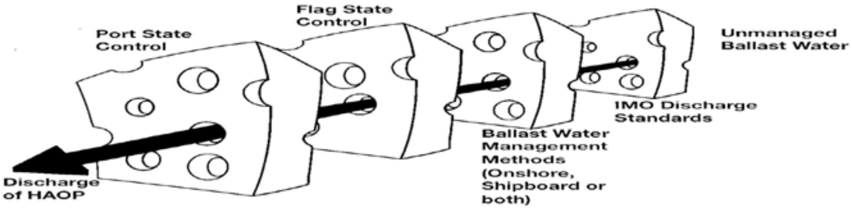


Figure 2. Metaphorical Swiss-cheese model of human-induced barrier for ballast water management (modified from Reason *et al*. [14]; [15]).

Reason [14] postulates that each barrier has some likely weaknesses or holes. These weaknesses or holes once they are aligned by chance could result in the occurrence of an accident

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or in the case of this study, an invasion [15]. The SCM is therefore used in risk analysis and risk management in aviation, engineering and healthcare. It was originally propounded by Dante Orlandella and James T. Reason of the University of Manchester, and has since gained widespread acceptance. It is sometimes called the cumulative act effect.

Collins *et al*. [16] used the SCM to analyze the effectiveness of a World Health Organization (WHO) surgical safety checklist designed to reduce the incidence of wrong-site surgery. Lubnau and Okray [17] also applied the model to the engineering of firefighting systems, aiming to reduce human errors by "inserting additional layers of cheese into the system", namely the techniques of Crew Resource Management. The SCM and two other systemic accident analysis methods were used by Underwood and Waterson [18] to carry out a comparative systemic analysis of the derailment of a train at Grayrrig. The outcome of the study establishes further the viability of SCM as a viable model of accident analysis. Li and Thimbleby [19] introduced a variant of the Reason's SCM called 'the hot cheese model'. The hot cheese model is a more realistic model, as they represent defense layers as active and passive. The model is more flexible and therefore allows for in depth discussion. Reason [15] identified four failure domains, and these are: organizational influences, unsafe supervision, preconditions and specific acts. These domains are the causes of the holes on our Swiss cheese.

In the case of ballast water management, some important examples of the Swiss cheese (or human-induced barriers) that are installed come in the form of policies from the IMO like the discharge standards (D-1 and D-2) of the ballast water management convention (BWMC), treatment or management systems installed either onboard the ship or onshore, flag and port state control monitoring systems (Figure 2).

2.3 Tens rule

The 'tens rule' is a biological statistical rule on biological invasion propounded by Williamson and Fitter [20]. This rule explained that invasion occurs with a statistical regularity of one tenth for each transitional stage, from *introduction* through *establishment* and ultimately *invasion* stages. For the purpose of this work the 'tens rule' can be explained thus: that for species entrained in a ballast water tank and imported into a new environment, only a tenth (1/10) will be *introduced* into a new environment, and for the introduced species only a tenth of them will become *established* in the new environment. For the species established only a tenth of them will become *pestiferous* or *invasive*. It means therefore, that only 1/1000th of species survive the transition from entrainment into the ballast water tank to invasion. Williams and Fitter (1996) were able to explore the characteristics of exotic species using ecological flora data and discovered species abundance as a key variable.

Using mammals and birds, Jeschke [21] found that strong conclusions cannot be made about the 'tens rule' as well as invasibility of islands and continents because of the incomplete records of species introduction available. The arrival of exotic species in a new area increases with proximity to ports [22]. One could therefore say that biological invasion is but the intended or unintended consequence of economic activity [23]. These generalizations have been shown to be useful for predicting the fate of introduced birds, terrestrial plants and insects [7] and shall be used in this study to show how it can be used to determine the bio-security risk of a ship visiting a port.

The AQIS ballast-water risk assessment [24] defines ballast water risk as

$$\text{Risk}_{\text{species}} = p(\omega).\ p(\phi).\ p(\psi).\ p(\upsilon) \quad (1)$$

where $p(\omega)$ = probability of donor port contamination

$p(\phi)$ = probability that vessel is infected with organisms

$p(\psi)$ = probability that species survives vessel's journey

$p(\upsilon)$ = probability that the species will survive and become invasive in the new environment

2.4 The precautionary principle

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Principle 15 of the Rio declaration codified at an international level the precautionary principle, which stipulates that actions to prevent serious or irreversible harm to the environment should be encouraged especially where there is either a lack of or insufficient scientific information on the potential to harm of our inaction. The precautionary principle states that the burden of proof for the potentially harmful action by a proponent rests on the assurance of safety from the proponent and that when there are threats of serious damage, scientific uncertainty must be resolved in favour of prevention [25].

Jaric and Cvijanovic [26] proposed a Precautionary Principle (PP) approach in managing species introduction, because according to them the 'tens rule' might be more of an indicator of our lack of understanding of the impacts that established introduced species produced than the actual ratio of such species that produces the undesirable impacts. The outcome of the analysis by Taleb *et al*. [27] however, concludes that PP is important only for limited set of contexts and can be used to justify only a limited set of actions.

However, as an extension and for the purpose of this study, PP presupposes that all organisms are potential invaders once they are translocated to a new clime that satisfies the preconditions for invasion in section 1.2. This is because any species removed from its native range and introduced to a new area has the potential to become an invasive species [28].

3. MATERIALS AND METHODS

Three sampling stations were set up at each of Port Harcourt Harbour (PHH) and Okrika Oil Terminal (OKOT), making a total of six (6) sampling stations. The choice of the stations was based on the fact that they are the major import and export terminals along Bonny Estuary in Nigeria. Ballast water samples were collected from four ships; two each berthing at PHH and OKOT. Surface water samples were collected from each of the stations. Sampling of the ballast water was done using standard IMO G-2 Guidelines for Ballast Water Sampling Protocols; Outflow and Manhole Sampling Methods. Surface water samples were collected at PHH and OKOT stations by collecting surface waters at subsurface levels of 25-30cm depth. All collected water samples were filtered through 63µm mesh plankton net for phytoplankton and 100µm plankton net for zooplankton according to the methods of Smithsonian Environmental Research Centre. The plankton species were identified using the appropriate keys/texts [29; 30], standard bench references and a CD-ROM from UNESCO (2000). All the water samples were also analyzed for some physico-chemical parameters (Table 3) using the methods recommended by APHA [31].
One-way ANOVA was used to test for differences in plankton densities and ballast water physicochemical properties between stations. Where ANOVA models were found to be significant, unplanned multiple comparisons (using Tukey and unpaired t-test) were used to differentiate group differences. Correlation analyses were also carried out to determine the relationship between the physico-chemical parameters and plankton abundance (example in Figure 3).

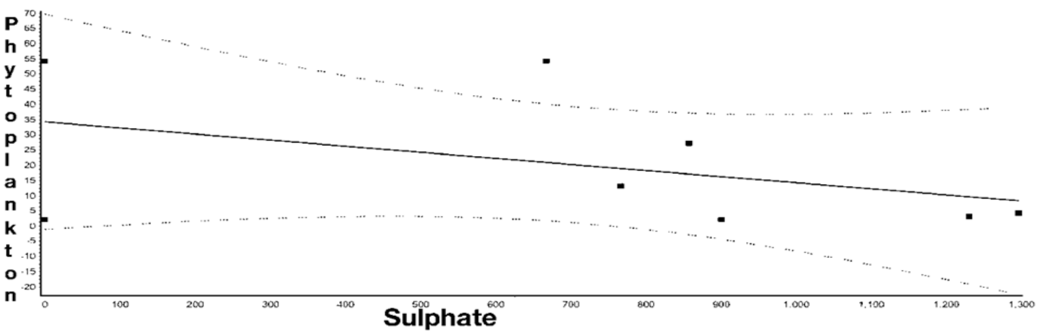


Figure 3. Total phytoplankton density log (mg/l) as a function of sulphate.

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4. RESULTS AND DISCUSSION

4.1 Results

4.1.1 Plankton numerical count

The results of biological sampling (Tables 1and 2) indicated a total of 30 species made up of 4 major taxonomic groups, namely bacillarophyceae, cyanophyceae (both phytoplankton), copepoda and rotifer (both zooplankton).

Table 1. Taxa numerical count

	Bacillarophycae	**Cynophycae**	**Copepoda**	**Rotaria**
PHH	39	15	2	0
OKOT	21	6	7	0
Vessel A	4	0	0	0
Vessel B	7	6	0	0
Vessel C	2	1	0	1
Vessel D	2	0	0	0
Total	**75**	**28**	**9**	**1**

Table 2. Plankton numerical count

	Phytoplanktons	Zooplanktons
PHH	54	2
OKOT	27	7
Vessel A	4	0
Vessel B	13	0
Vessel C	3	1
Vessel D	2	0

A total of 113 individuals of the various species were recorded (Tables 1 and 2). The results did not show any significant difference in the relative abundance between surface waters of PHH and OKOT using t-test (t_{cal} = 1.084, df =10, $p \geq 0.05$). Repeated measures ANOVA shows significant difference between the different species sampled (i.e bacillarophycae, cynophycae, copepoda, rotatoria). The variation is significantly greater than expected by chance (Figure 4: Repeated ANOVA, Fcalc=3.856; df=3, 5, p=0.0315).

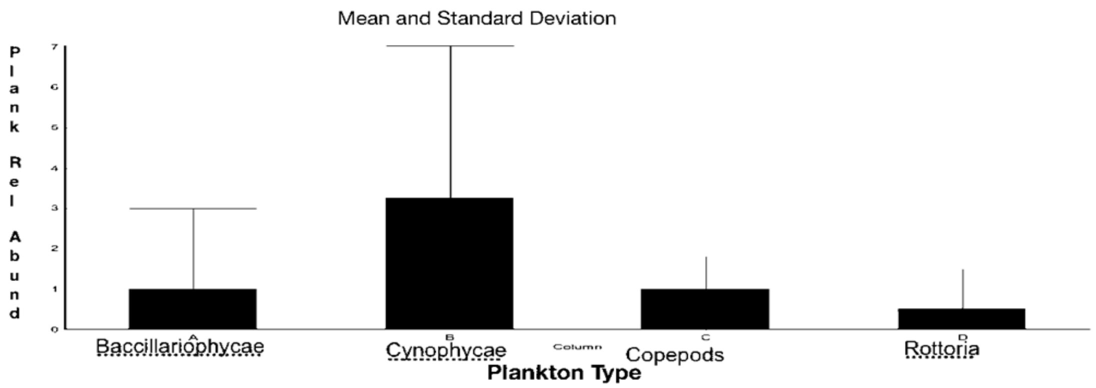


Figure 4. Summary of mean and SD total plankton relative abundance observed in PHH and OKOT.

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Also, no significant difference in the relative abundance of total plankton between ballast waters of all sampled vessels was observed (Figure 5: ANOVA, t_{cal} = 2.268, df=3.3, p≥0.05). Comparison between zooplankton and phytoplankton abundance using the impaired t-test showed a slight significant difference between the two means (t_{cal} = 1.847, df = 10, p≥0.05). The results also showed a strong positive correlation between DO levels and zooplankton abundance (r = 0.8317, p≥0.01). There is also a strong positive correlation between BOD and zooplankton abundance (r = 0.8532, p≥0.01). For phytoplankton, of all the physico-chemical parameters, only BOD showed positive correlation, although weak (r = 0.0723). For zooplankton abundance only BOD, sulphate, and nitrate showed significant linearity as well as correlation, whereas for phytoplankton abundance, sulphate and all the other parameters measured showed correlation and linearity (Figure 3).

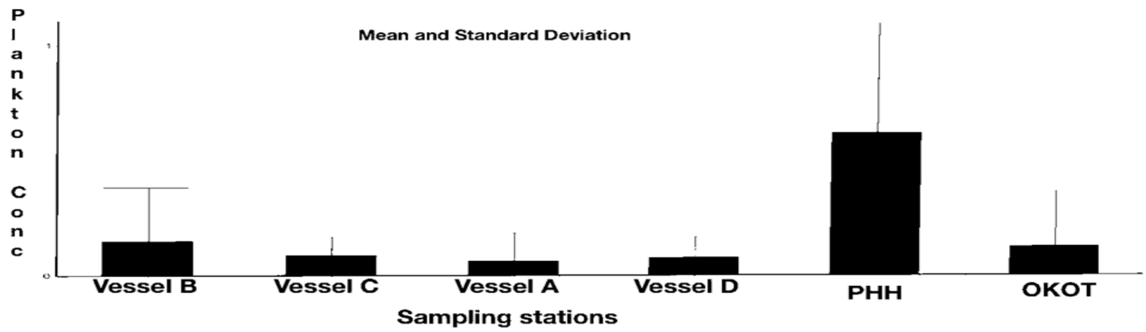


Figure 5. Summary of mean and SD total plankton relative abundance observed in ballast water of vessels as well as Terminals (PHH and OKOT).

4.1.2 Physicochemical Parameters

The results of the physico-chemical parameters (Table 3) did not show any significant difference between PHH and OKOT surface water (t_{cal} = 1.689, df = 3 p≥ 0.05).

Table 3. Physico-chemistry of sampled stations

S/N		pH	Elect. Cond (ms/cm)	Turbidity (NTU)	Salinity (psu)	Tempt (°C)	DO (mg/l)	BOD (mg/l)	SO_4^{-2}	PO_4^{-3}	NO_3^-
1	PHH	6.91	26700	14	16.5	28.9	4.1	3.2	668.0	<0.05	0.07
2	OKOT	7.54	31200	5	19.6	30.6	9.7	5.7	858.1	<0.05	0.07
3	Vessel A	7.27	32100	56	20.1	31.3	4.9	3.2	901.3	<0.05	<0.05
4	Vessel B	6.76	28200	18	17.5	29.6	2.4	0.8	766.8	<0.05	<0.05
5	Vessel C	8.01	50200	12	33.0	29.7	6.5	1.6	1231.0	<0.05	<0.05
6	Vessel D	6.63	49600	2	32.6	29.5	4.1	2.4	1296.9	<0.05	0.07

4.2 Discussion

The goal of ballast water management is to reduce the risk of organisms' introduction by removing or inactivating those organisms resident within the ballast water tanks of ships.

The probability of invasion can be determined using the established methodology of simple probability law and the 'tens rule'. The risk variables that can be easily measured from the data in this study are $p(\psi)$ and $p(\upsilon)$. Probability of donor port contamination $p(\omega)$ and entrainment into the ballast water tank $p(\phi)$) of HAOP is assumed to be one (1) each following the precautionary

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principle. The entire chain from uptake of HAOP into ballast water tank $p(\omega)$ and $p(\phi)$) to voyage survival rate $p(\psi)$ and ultimately invasion $p(\upsilon)$ is a numbers game known as 'propagule pressure'. The propagule pressure is directly proportional to the probability of invasion (Equation 1).
From a total of 30 species identified in this study, *Nitszchia lineans* and *Triceratuim* sp.(both phytoplankton) and *Playtias* sp (a zooplankton) are the only species not found in either of the samples from PHH and OKOT (Tables 1, 2 & 3). Applying the 'tens rule' the probability of these species being invasive will be p = 0.003. This means that these three species could be introduced into PHH. The implication of this will be that though the probability of the invasiveness of these species is quite low, they still pose some level of security risk to the environment as long as the invasion preconditions in section 1.2 are satisfied. This is especially so for vessels A and B whose salinity and electrical conductivity levels matches that of PHH and OKOT the most (Table 3). The treatments that are most appropriate for a class of organisms with size >50 μm should be assumed applicable for all the zooplanktons and on the other hand treatments methods that are appropriate for organisms in the 10 – 50 μm size class should be applicable to phytoplankton [32].

For the zooplankton population sampled on the other hand, only 1 organism has the likelihood of being introducible. It therefore follows that for the vessels sampled, the probability of introducing a non-existing species is 1 and the probability of that species becoming invasive following the tens rule is p=0.001. This means that the ships sampled did not pose any bio security risk to PHH, or Bonny Estuary at the period of the study.

By assuming the 'precautionary principle' where all organisms are assumed to have invasive potentials unless proven otherwise, the organisms identified from the host environment (i.e PHH and OKOT) are all potential invasive organisms and also have a probability of being entrained into the ballast water tank of a ship and are ultimately introduced into the next port of call [28]. By applying the 'tens rule' however, 9% (p=0.09 at *a priori* α-level of 0.05) of the organisms will stand the chance of going through the process of *introduction*, *establishment* and ultimately becoming *invasive* or *pestiferous*. The probability of species found in sampled visiting ships (Vessels A, B, C and D) becoming invasive on the other hand is much more insignificant at p=0.043. By introducing a pre-voyage onshore treatment system for ballast water (i.e. pre-voyage treatment of harbor water for ships), these probabilities are further reduced to insignificance. In accordance with the 'tens rule' the propagule pressure of organisms within the ballast water tank of the ship on arrival at the next port of call (NPOC), might not be sufficient to establish an invasive or pestiferous community in the new environment as long as the ballast water is treated. This is because the propagule pressure reduces with every protective layer of treatment added to the treatment system including the ship's own ballast water tank which serves also as an additional protective layer or barrier against introduction in the next port of call (NPOC).

5. CONCLUSION

The seaport as an invasion front is home to genetically dispersive organisms. In this paper, with the aid of field data collected from four ships (Vessels A, B, C and D) and two seaports (PHH and OKOT), four established theories were used to determine the bio-security levels of the four visiting ships to the two seaports. Based on the precautionary principle for example, it is assumed that all organisms are potentially invasive once removed from their host environment to a new one. This new environment must satisfy a certain set of environmental conditions for the inoculated organisms to become established and ultimately invasive. Another theory, the theory of spatial sorting, states that these organisms found in seaports have or are genetically developing higher propensity for dispersive or hitchhiking behavior than their ancestors. Once the ballast water containing the organisms is subjected to treatment, the metaphoric Swiss cheese or a human-induced barrier is introduced. The Swiss cheese in this case is ballast water management. This

management process is comprised of a series of barriers in the form of policies (like D-1 and D-2 standards of BWMC), activities and technologies to achieve safe discharge of ballast water and sediments from ships on international voyage. Finally, the impact of these introduced barriers on bio-security follows a statistical regularity of the 'tens rule'. The entire process chain with respect to these theoretical concepts showed how the capacity to introduce organisms with invasive capacity into a new environment is systematically impaired when, treated ballast water is discharged by ships into an environment. A further application of the statistical characterisation of the 'tens rule' logic showed that the resultant propagule pressure posed only a significantly low risk of species introduction to PHH, OKOT or the Bonny Estuary. This outcome could be sufficient to satisfy the numeric requirements of regulation D-2 of the Ballast Water Management Convention of IMO.

References

[1] Battle, J. (Ed)., 2009. Silent invasion: The spread of marine invasive species via ships' ballast eater. *WWF for a Living Planet*. Retrieved April 14, 2016 from http:www.wwf.se/se/source.php/1254140/silent invasion_2009.pdf.

[2] Gollasch, S., & Leppakoski, E., 2007. Risk assessment and management scenarios for ballast water mediated species introductions into the Baltic Sea. *Aquatic Invasions*, **2**(**4**), 313-340.doi:10.3391/ai.2007.2.4.3.

[3] Global Ballast Water Management Program (GloBallast), 2004. Ballast water treatment R & D directory. 2nd ed. International Maritime Organization. London.

[4] Shine, R., Brown, G.P., & Phillips, B.L., 2011. An evolutionary process that assembles phenotypes through space rather than through time. *PNAS*, **108**(**14**), 5708-5711doi:10.1073/pnas.1018989108.

[5] Kazumi, J. 2007. Ballast water treatment technologies and their application for vessels entering the Great Lakes via the St. Lawrence Seaway: Options to Eliminate Introduction of Nonindigenous Species into the Great Lakes. *Phase 2 Transportation Research Board and Division on Earth and Life Studies*, University of Miami, Miami, Florida. Retrieved September 12, 2010 from http://www.onlinepubs.trb.org/sr291

[6] Dobroski, N., Takata, C., Scianni, C. & Falkner, M., 2007. Assessment of the efficacy, availability and environmental impacts of ballast water treatment systems for use in California waters. *Produced for the California State Legislature*, 224.

[7] Humphrey, D.B., 2008. Characterizing ballast water as a vector for nonindigenous zooplankton transport. A Thesis Submitted in Partial Fulfillment of the Requirement for the Degree of Master of Science in the Faculty of Graduate Studies (Oceanography). The University of British Columbia (Vancouver), September 2008.

[8] Gollasch, S., Lenz, J., Dammer, M., & Andres, H.G., 2000. Survival of tropical ballast water organisms during a cruise from the Indian Ocean to the North Sea. *Journal of Plankton Research* **22**(**5**), 923-937. Retrieved February 6, 2011 from http://plankt.oxfordjournals.org/content/22/5/923.full.pdf+html.

[9] Wonham, M.J., Walton, W., Ruiz, G.M., Frese, A.M & Galil, B.S., 2001. Going to the source: role of the invasion pathway in determining potential invaders. *Marine Ecological Program Service* **215**,1-12. Retrieved August 29, 2009 from http://www.int-res.com/articles/meps/215/m215p001.pdf.

[10] Kuroshi, L.A., 2012. Onshore ballast water treatment stations: A harbour specific vector management proposition. Thesis Submitted to the World Maritime University, Malmo, Sweden for the Award of a Master of Science Degree.

[11] International Maritime Organization (IMO), 2005. International convention for the control and management of ships' ballast water and sediments. Report of the Marine Environment Protection Committee on its fifty-third session (MEPC 53/24/Add.1) London. Retrieved September 11, 2010 from http://docs.imo.org/

[12] Urban, M. C., Phillips, B. L., Skelly, D. K., & Shine, R., 2008. A toad more traveled: The heterogenous invasion dynamics of cane toads in Australia. *The American Naturalist*, **171**(**3**), E134-E148. doi:10.1086/527494

[13] Lindstrom, T., Brown, G.P., Sisson, S.A., Phillips, B.L., & Shine, R., 2013. Rapid shifts in dispersal behavior on an expanding range edge. *PNAS*, **110**(**33**), 13452-13456.doi:10.1073/pnas, 1303157110.

[14] Reason, J., 1990. The Contribution Of Latent Human Failures To The Breakdown Of Complex Systems. Philosophical Transactions of the Royal Society of London. *Series B, Biological Sciences* (1934-1990), 475-484.

[15] Reason, J., Hollnagel, E., & Paries, J., 2006. Revisiting the Swiss cheese model of accident. *European Organization for the Safety of Air Navigation*, **13**(**6**), 1-35.

[16] Collins, S., Newhouse, R., Porter, J., & Talsma, A., 2013. Effectiveness of the surgical safety checklist in correcting errors: A literature review applying Swiss Cheese Model. *ACORN: Official Voice of Peri Operative Nursing*, **10**, 10016-10016.

[17] Lubnau, T., & Okray, R., 2004. Crew Resource Management for the Fire Service. PennWell Books. Tulsa.

[18] Underwood, P., & Waterson, P., 2013. Systems thinking, the Swiss Cheese Model and accident analysis: A comparative systemic analysis of the Grayrigg train derailment using the ATSB, AcciMap and STAMP models. *Accident Analysis & Prevention*, **68**, 75-94.

ISBN: 978-960-6865-94-7

[19] Li, Y., & Thimbleby, H., 2014. Hot cheese: A processed Swiss cheese model. *Journal of Royal College of Physicians,* Edinburgh, **44**(**1**), 16-21. Retrieved March 12, 2015 from http://www.ncbi.nlm.nih.gov/pubmed.
[20] Williamson, M., & Fitter, A., 1996. The characters of successful invaders. *Biological Conservation*, **78**, 163-170.
[21] Jeschke, J. (2009). Across islands and continents, mammals are more successful invaders than birds. Diversity and Distributions- *A Journal of Conservation Biogeography*, **14**(**6**), 913-916.
[22] Jeschke, J. & Strayer, J., 2005. From The Cover: Invasion success of vertebrates in Europe and North America. *Proceedings of the National Academy of Sciences,* **102**(**20**), 7198-7202.
[23] Perrings, C., 2001. Mitigation and adaptation strategies for the control of biological invasions. *Ecological Economics,* **1**(**3**), 315-325.
[24] Hayes, K.R., & Hewitt, C.L., 1998. Risk assessment framework for ballast water introductions. *Centre for Research on Introduced Marine Pests. Technical Report. CSIRO Marine Laboratories,* Hobert.
[25] Goldstein, B., 2001. The Precautionary Principle Also Applies to Public Health Actions. *American Journal of Public Health*, **91**(**9**), 1358-1361. Retrieved March 11, 2009 from *http://www.ncbi.nim.nih.gov/pubmed* .
[26] Jarić, I., & Cvijanović, G., 2005. The Tens Rule in Invasion Biology: Measure of a True Impact or Our Lack of Knowledge and Understanding? *Environmental Management*, **102**(**20**), 979-981.
[27] Taleb, N., Read, R., Douady, R., Norman, J., & Bar-Yam, Y., 2014. The precautionary principle: Fragility and black swans from policy actions. Extreme Risk Initiative-*NYU School of Engineering Working Papers*.
[28] Veldhuis, M., Hallers, C., Riviere, E.B., Fuhr, F., Finke, J., Steehouwer, P.P., Star, I., & Sloote, C., 2010. Ballast water treatment systems: "Old" and "New" Ones. *Emerging ballast water management systems* (eds.N. Bellefontaine; F. Haag; O. Linden, and J. Matheickal) 26-29 January, 2010, Malmo, Sweden Vol. III, 97-105.
[29] Newell, G. E., & Newell, R. C., 1977. *Marine Plankton: A practical guide* (5th ed.). London: Hutchinson Educational.
[30] Needham, A. E., 1974. *The significance of zoochromes*. Springer-Verlag, New York.
[31] APHA, 1998. Standard methods for the examination of wastewater (20^{th} Ed.) *American Public Health Association,* 1193 (1998), New York.
[32] Dobroski, N., Scianni, C., Gehringer, D. & Falkner, M., 2009. Assessment of the efficacy, availability and environmental impacts of ballast water treatment systems for use in California waters. Produced for the California State Legislature, 88..

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Measures rehabilitation and management of riparian ecosystems and riparian forest Agras Lake (GR1240004), Macedonia, Greece

N. Grigoriadis[1*], G. Efthimiou[2], S. Grigoriadis[1]

[1] Forest Research Institute, NAGREF, 57006, Thessaloniki, Greece.
[2] Department of Forestry and Natural Environment Management, Technological Educational Institute of Sterea Hellas, 36100, Karpenissi, Greece.

*Corresponding author: Email: grig_nick@fri.gr

Abstract

Riparian ecosystems support great biodiversity but in the same time are accepting intense pressures from human activities which often depending of intensity they degrade the quality and ecologically. The conservation, rehabilitation and restoration of them is a main concern for the protection of their ecological functions and biodiversity of the region. As study area was chosen Lake Agra in Pella (Macedonia), which belongs to the European ecological network Natura 2000 as SCI and SPA area, with code GR1240004.

The purpose of this paper is to present the restoration projects and management measures in wetland ecosystems of Lake Agra that took place under the Life-Nature program implementation in this wetland, or the rectification of some habitats or the re-establishment of riparian forest. to restore biodiversity and their operation and to improve the ecological value of the wetland.

Keywords: management; riparian ecosystems; Agras Lake; rehabilitation; riparian forest.

1. INTRODUCTION

Wetlands are ecosystems that support high biodiversity. At the same time they receive heavy pressure from human activities that take place in the surrounding area. Depending on the intensity of the human activities, wetlands show a varying degree of degradation. One of the key management measures required by the Ramsar Convention, of which our country is a member, is the restoration of wetland ecosystems and their functions.

One of the most important ecosystems of the wetlands are the riparian forests and the riparian vegetation [1, 2]. Applications and rehabilitation programs of the riparian forest vegetation have been implemented in a number of wetlands of our country such as Lake Volvi, Nestos, Kastoria Lake, Lake Agras etc. Lake Agras was chosen as a study area, a semi-natural wetland in the prefecture of Pella in Macedonia. It is a part of the European ecological network NATURA 2000, featured as a Site of Community Importance (SCI) and Special Protection Area (SPA) with code GR1240004. It is also designated as a Wildlife Refuge [3].

The purpose of this paper is to present an integrated management of ecosystems in the wetland of Agras with the implementation of management measures for its habitats.

2. RESEARCH AREA

The wetland of Agras (Figure 1a) was selected as a research area. It is a semi-natural lake that is integrated in the European network Natura 2000. It is located in Pella, Macedonia Greece [4], 7 Km

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from Edessa and extends to 600 ha. It takes its name from the hero of the Macedonian wars Captain Agra. During the ancient times, the marshy areas of the region was known as Tiavou Marsh [5]. In the region of Lake Agras, 16 types of natural habitats have been recorded (Figure 1b), 12 of which belong to terrestrial and 4 of them to wetland ecosystems [6, 7].

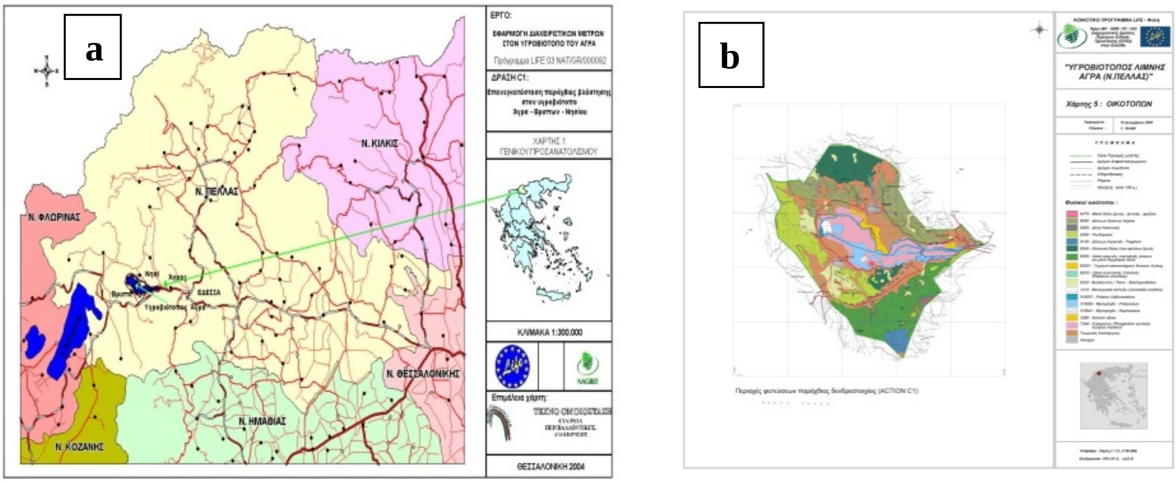


Figure 1. Location map (a) and habitat's map (b) (Platis et al. 2000).

2.1 Riparian vegetation

The vegetation types that appear in the study area are shrub lands, especially reeds, riparian forests and wet meadows. Until the recent decades and prior to the program implementation, the riparian forests had shrunk significantly. The main riparian forest species are willows (*Salix cinerea* and *S. alba*) and poplars. The recorded species in the riparian vegetation is 38 [8]. The existence of orchids and irises, shows great ecological interest. Three types of orchid [6] have been recorded. Reeds appears along the shores of the lake (*Phragmites sp*.), Straw (*Typha sp*.), Rushes (*Juncus sp*.), Nutsedge (*Cyperus sp*.). In over all, there have been recorded 325 taxa [5], while in the previous survey of Karagianakidou et al. (2003) there have been recorded 309 taxa, from 72 families and 182 genera. The eight habitats that were originally found in the lake with the codes of Natura2000 were: 3150, 72A0, 7210, 92A0, 92C0, 6420, 5350 and 924A. The riparian vegetation that was recorded in the area is a) woodland galleries with *Salix alba* and *Populus alba* (92AO) where *S. cinerea, Humulus lupulus, Ulmus minor, Rubus sp., Juglans regia, Cornus sp.* can be found and b) forests of *Platanus orientalis* (92CO) with *Populus sp., Rubus sp., Ulmus sp.* [8]. A map with the vegetation type at Agras wetland is given in Figure 1b, and 2.

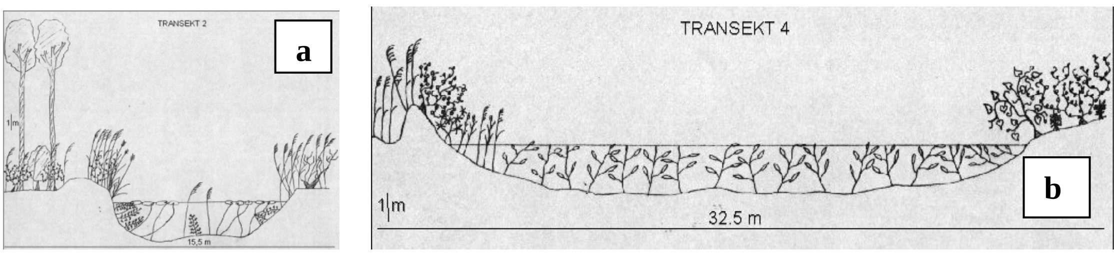


Figure 2: A scheme with submergend rhizophytes in the water and helophytes at the old course of the River Edessaios (a or Transect 2) and at the channel banks (b or Transect 4) of wetland (Grigoriadis 2009).

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2.2 Fauna

The fauna (mammals, reptiles and fishes) that is present in the lake in addition to the bird diversity that inhabits the lake is rich.

About 133 species of birds have been recorded in nine habitats of the lake [7]. The most *Populus* species is the coot with great difference from other species. The number of species that use the area during the winter does not show sharp fluctuations [9]. Over 68 species of birds use the wetland [5]. Most species prefer the central part of the wetland [10].

The presence of coypu (*Myocastor corypus*) that has been introduced by man, and a species of native lobster (*Astacus fluviatis*) that are protected by the Berne and Barcelona and CITES Conventions should be noted.

2.3 Water

There were three lakes in the area, the lake of Edessa, which is not currently present, the Nisi Lake and the Vegoritida Lake. The Nisi Lake grew in size and became Lake Agras, after human interventions, the dam construction from the Public Power Corporation in 1955, and irrigation channels. Lake Agras is being fed by springs of the Edesseos river and until 26 years ago (1990) was hydrologically dependent from Lake Vegoritida [5]. About 5000 ha of agricultural land uses water from the irrigated Agras Lake. The total area of the wetland Agras- Nisi -Vryta can be estimated to 4,351 ha of which the water surface occupies the $1/10^{th}$ while the half the area of the wetland is permanently flooded and about $1/6^{th}$ is seasonally flooded [11].

2.4 Geology

The substrate of the lake consists of peat with predominance of alluvial deposits tertiary period. The region is dominated by limestone. The accumulation of peat in the basin can be15 m thick [12]. It was mentioned as follows: «*since the last glacial, limnotelmatic and pure telmatic conditions, controlled mainly by karstic springs and partly by surface waters, favored peat formation*".

2.5 Human activities

In the wider region of the lake there can be found extensive tree crops (especially cherries) and poplars. The poplars spanning 201.5 ha [11]. The stock raising is also developed in the area. In the past years there was intense fishing activity in the lake, but now due to the reduction of the fish population, it has been diminished as an activity. Tourism has been developed during recent years in the wetland.

2.5 Problems

The study area is being degraded by several issues. Due to the drop in the water level of the Vegoritida Lake, the waterway supply to Lake Agras has stopped. The intensive farming with the use of fertilizers and pesticides degrades the quality of the waters of the lake. The observed increase of reeds is a consequence of the sedimentations occurring at the lake, with obvious reduction of the fish population. Also, the lack of food reduced the population of birds.

Disturbance by humans probably contributed to the migration of the bird populations in the interior parts. This was observed in all parts of the lake, but mainly in the western and eastern part [10].

Eutrophication problems, increased reed and priority species discomfort have been recorded in the lake. By monitoring the changes of the wetland types a growth of agricultural crops around the lake at the expense of natural bushy vegetation and an expansion of 9% of the reed in wet meadows has been recorded [7, 13].

Threats have been recorded for the flora (orchids) and the riparian vegetation in the area, such as intense grazing, fire, vegetation cutting and forage [6].

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The riparian vegetation has been shrunk by the intensive agriculture, grazing, sewage and the waste that are dumped in the water body of the lake [8].

3. MEASURES REHABILITATION AND MANAGEMENT OF RIPARIAN ECOSYSTEMS

3.1 Measures for the riparian forest vegetation

For the restoration and the enrichment of the riparian forest vegetation, plantings took place, using planting material from the study area. The riparian forest species that have been planted and their number is given in Table 1.

The aim of this measure was to restore the structural heterogeneity in vertical (floor number of trees and shrubs) and horizontally. The choice of planting material took into account the morphological (genetic) diversity to simulate the natural situation as much as possible. This means planting more than one species (e.g. species of willow, alder, poplar, plane) that have been as locally sourced as possible. These plantings were made in appropriate positions, both regarding what the plant needs, but also what the bird needs.

In Agras a total of 910 trees were planted in 2006 in seven positions (1, 8, 9, 16, 17a, 17b, 18) of the wetland core as shown in Figure 4 and in an area of a total surface of 2550 m^2.

Table 1. Riparian forest species and number planted.

Species	No (2006)
Salix alba	344
Salix cinerea	505
Platanus orientalis	61
Total	910

3.2. Reed bed management

A reed bed management measure took place due to the large area that the reeds had captured at the water surface of the lake. The primary management measure that took place was the experimental cutting. The cutting of the reeds took place both during summer and winter in an area of approximately 1 ha [14, 15].

3.3 Measures for the riparian avifauna

To help the birds of the region, floating islands were designed and built to provide ideal places for resting, nesting and breeding of the species that live, winter and breed in the lake.

3.4 Measures for the recovery of the biodiversity of wetland

A number of interventions have been made aiming to improve and restore the riparian ecosystems of the region, with the aim of improving the wetland habitats [6, 16, 17].

To make the wetland friendlier for the fish fauna and the crawfish, channels that enabled the free movement of water were created, so that the water is well oxygenated. This way the habitats were improved for aquatic organisms and in particular for the endemic crayfish. A tighter control of fishing was introduced, especially during the breeding season.

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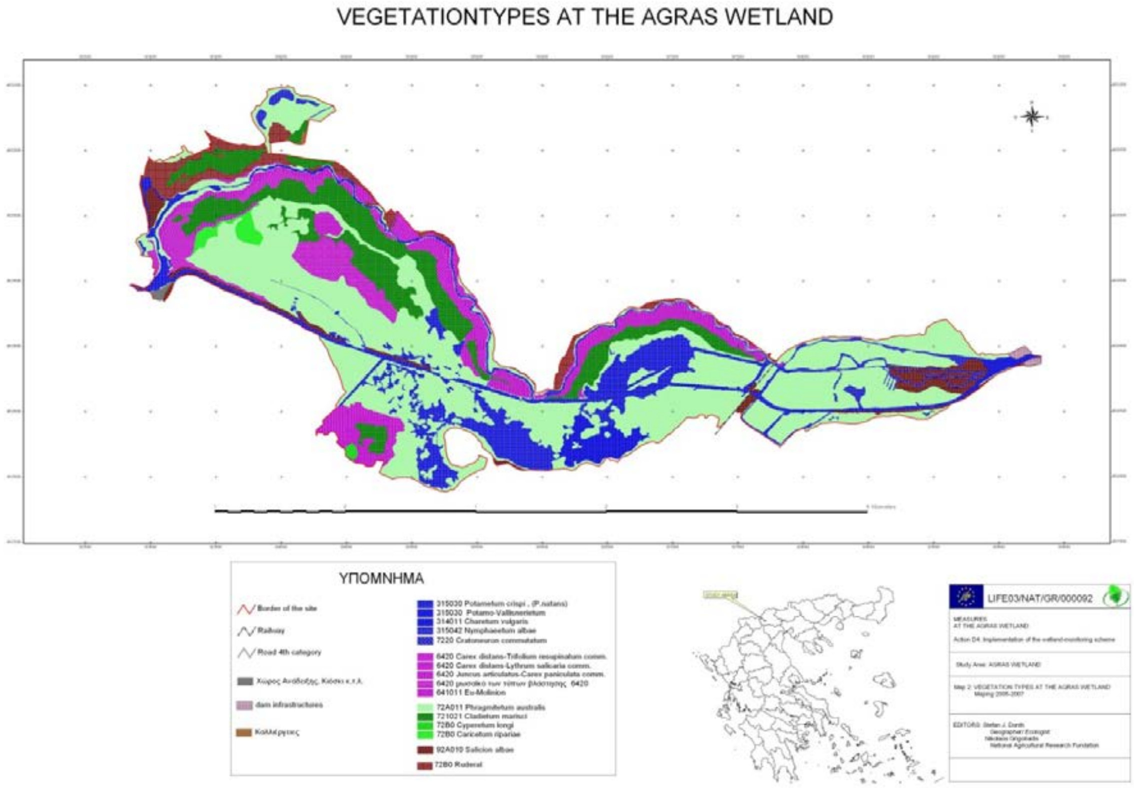


Figure 3: Map of the study area showing habitat distribution and relevé locations (Grigoriadis 2007).

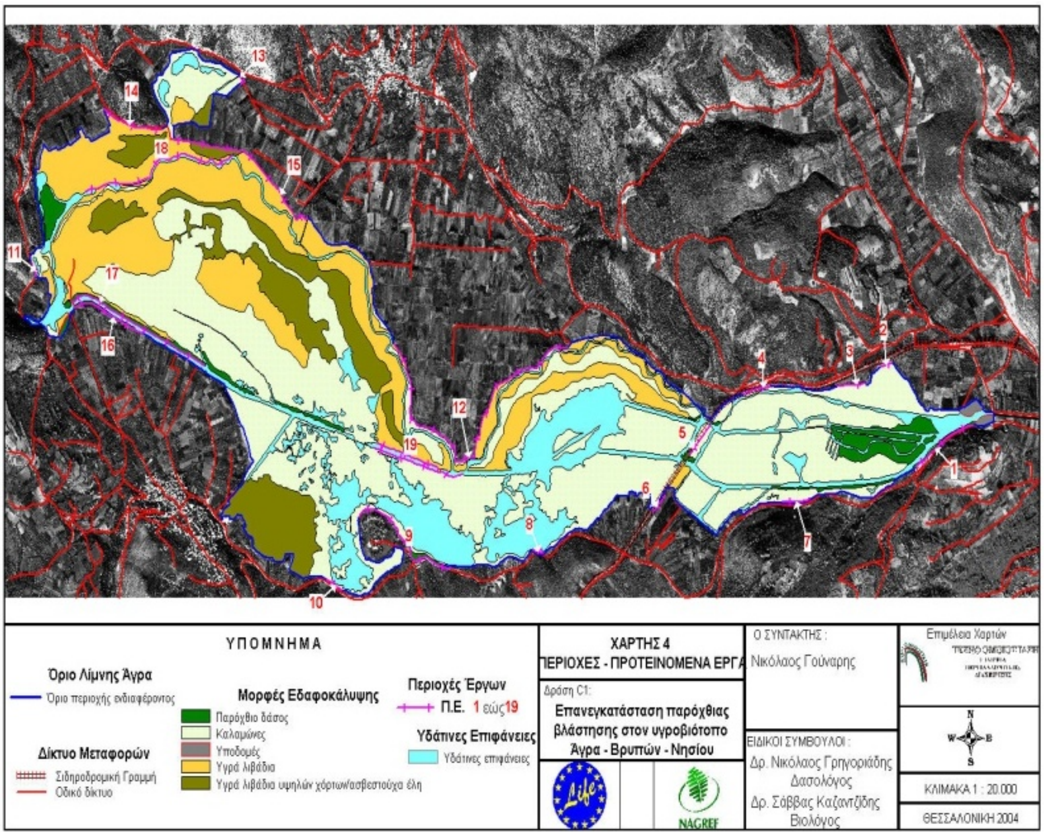


Figure 4. Map of the riparian vegetation restoration actions of the wetland of Agras Lake (Grigoriadis 2007).

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3.5 Protection measures of the wetland

Keeping the wetland safe was possible with hiring seasonal guards and the cooperation of the competent governmental and non-governmental services, such as the Forest Service, the Fire Department, the wild life warden, the Municipality of Edessa, and the Hunting Federation of Macedonia and Thrace.

3.6 Measures for monitoring the wetland

The program provided the monitoring of habitats of the wetland Agras, emphasizing in vegetation habitats, the bird life and some of the hydrological characteristics.

3.7 Measures for the ecotourism exploitation of wetland

Under the Life Nature 2000 program, various infrastructure were created for the use and promotion of the lake ecosystems and to attract visitors. The wetland is located on the main road of Thessaloniki-Edessa-Florina and near the ski center of Voras (Kaimak-tsalan).

3.7.1. Measures for ecotourism development

The ecotourism infrastructure created in the wetland area of Agras includes;:

1. Two ecotourism stands; one by the lake and one in the city of Edessa near the waterfalls for the distribution of printed material and providing information to visitors.
2. Navigation paths and natural environment interpretation
3. Observatories for the fauna-flora and the landscape
4. Reception for the visitors, for video projections and information center
5. Guest house for accommodation in Vrytta and
6. Signs to inform the public at key points in the area.

3.7.2. Measures for environmental education

In the context of implementation of the second program Life Nature, information material about the flora and the fauna of the Agras Lake was compiled and printed, and an environmental education package for schools was created. Also, a room was equipped with audiovisual equipment for video projection and conducting lectures to groups of students visiting the area. The information hall is located next to the dam.

4. CONCLUSIONS

The implemented monitoring and rehabilitation program of the riparian ecosystems of wetland Agras, is one of the few that have been implemented in the Greek territory and it could be a model for integrated management of wetland protected areas.

The positive outcome is that the program that was implemented in the wetland of Agras, sensitized the stakeholders and the local population. Through this program, they were informed about the multiple functions and benefits of the operation of sustainable management and designation of a wetland as an SPA area in the European network of NATURA 2000 and as an ecotourism destination.

References

[1] Efthimiou, G. 2000. Structure analysis, dynamic and ecological interpretation of riparian forests of Nestos. PhD Thesis, School of Forestry and Natural Environment, Aristotelian University of Thessaloniki (AUTh), Thessaloniki, 407p. (in Greek).

[2] Efthimiou, G. 2012. The slenderness of the softwood Riparian forest species Salix alba L. and Salix fragilis L. in the protected area of Nestos Delta, Greece. *Journal of Ecology and the Natural Environment* **4 (1)**, 1-7.

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ISBN: 978-960-6865-94-7

[3] http://www.edessacity.gr. (accessed February 20, 2016).

[4] Grigoriadis N., Donth, S., Theodoropoulos, K., Elefteriadou, E. 2005. Establishment of a habitat monitoring system in Agras wetland (Pella, Greece). *Analli di Botanica*, **18**, 135-147.

[5] Kousouris, T.S. 2014. Lake Nissi, Edessa. In “the lakes of Greece, Macedonia”, **3(6)**, 56-62. (inGeek).

[6] Grigoriadis, N., Chasilidis, P., Theodoropoulos, K., Eleftheriadou, E., 2013. Preliminary results of the orchid’s monitoring in the habitat of “Mediterranean tall humid herb grasslands of the Molinio-Holoschoenion” (6420) of the wetland Agras (GR1240004). *Geotechnical Research Themes*, **22 (1),** 4-12. (in Greek).

[7] Platis, P., Grigoriadis, N., Papachristou, Th., Kasioumis, K., Hatzilakou, D., Dimalexis, A., Bousbouras, D. 2000. Special environmental study of a SPA (Management plan of the "Lake Agras" wetland). NAGREF, Thessaloniki. (in Greek).

[8] Karagianakidou, V., Papadimitriou, M., Platis, P., Iatropoulos, K. 2003. Contribution to the knowledge of the flora and the vegetation of wetland lake Agra. *Proceedings of the 3rd Panhellenic Rangeland Congress “Range Science and development of mountainous regions”*. September 4-6, Karpenissi, Greece, 271-277. (in Greek).

[9] Kazantzidis, S., Noidou, M. 2008. Research for aquatic birds in Greek wetlands, *NAGREF*, **31**, 4-7. (in Greek).

[10] Grigoriadis, S. 2009. The Birds in the wetland of Agra. Diploma thesis. School of Forestry and Natural Environment, Aristotelian University of Thessaloniki (AUTh), Thessaloniki 85 p. (in Greek).

[11] Fitoka, E., Kontos, N. 2002. Collection of inventory data for selected wetlands. Ministry of Environment, Physical Planning and Public Works and Greek Biotope / Wetland Centre. Thermi. 40 p. + xi annexes.

[12] Christanis, K. 1994. The genesis of the Nissi peatland (northwestern Greece) as an example of peat and lignite deposit formation in Greece. *International Journal of Coal Geology*, **26**, 63-77.

[13] Platis, P., Papachristou T., Trakolis D., Meliadis I., Grigoriadis N., Makras, A. 2004. Monitoring of vegetation types changes in the area of Lake Agra. *In Proceedings of the 4th Panhellenic Rangeland Congress “Pastures of lowland and upland areas-Lever rural development*.” November 10-12, Volos, Greece, 355-361. (in Greek).

[14] Grigoriadis, N. 2007. Final Report Program LIFE-NATURE 2003, Implementation Management measures in Wetland of Agras (LIFE03 NAT/GR/00092). (in Greek).

[15] Thomaidou, V. 2009. Plan of integrated interventions in wetlands, the case of the Agras lake. Master, Faculty of Engineering, AUTh, Thessaloniki, 112 p. (in Greek).

[16] Dimalexis, A. 2009. GR1240006 Lake and Dam of Agras. In the "Identification of compatible activities and the species designation of special bird protection areas" Env. Min., Athens, 39 p.

[17] Noidou, M., Kazatzidis, S., Grigoriadis, N., Dimalexis, A. 2007. The waterfowl ay Agras Lake and their protection measures. *Proceedings of the 13rd Panhellenic Forestry Congress “Range Science and development of mountainous regions*”. October 7-10, Kastoria, Greece, 389-393. (in Greek).

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The riparian ecosystems of Sperchios river, Central Greece. A survey of literature

G. Efthimiou[1*], E. Tsirekis[2], A. Mertzanis[1], A. M. Papadopoulos[1]

[1] Department of Forestry and Natural Environment Management, Technological Educational Institute of Sterea Hellas, 36100, Karpenissi, Greece.
[2] Forester MSc, 123 Timfristou str, 35100, Lamia, Greece.
*Corresponding author: Email: efthimiou@teiste.gr

Abstract

The Sperchios River is the most significant river in Central Greece. Many settlements grow along the valley and intense human activity Is observed that affects the riparian ecosystems. The Sperchios river area is a designatedto the European ecological network Natura 2000 (GR2440002).

The aim of this research is to record the literature till now of the Sperchios River up to the present day, to show the ecological importance of riparian ecosystems, to identify problems. The aim of this literature review is to highlight the ecological importance of the river ecosystems. Is important to mention that in the study area is located the largest natural riparian forest of *Platanus orientalis* in Greece.

Literature was recorded for the period 1950 - 2015 and found overall 166 papers, the 44.5% of which are announcements in journals and conferences. The earliest recorded reference was in 1838 by Gordon M.G. An increased interest in Sperchios is observed over the last 25 years (1990-2015) in which ¾ of the total publications published the in our study period. 41.6% of the publications concerning hydrology, hydrogeology and pollution while the scientific interest in the riparian vegetation and forests recorded in the last 5 years and accounts for 4.2% of publications. The survey is of great scientific interest in riparian ecosystems of Sperchios river

Keywords: Sperchios River; riparian ecosystems; management; riparian forest; protected area.

1. INTRODUCTION

The objective of the present study is to record the published literature over the last 65 years i.e., from 1950 until 2015. The Sperchios River flows through the homonymous valley, a location of significant importance for the ancient and natural history of Greece. The valley has several thermal springs most of which are located at the base of mountains Oiti and Knimi that emerge from the plains on the south, at north the foothills of Othris mountain with its local unique geology the valley on the west and south west is enclosed by the prominent Tymfristos mountain and the spectacular Vardousia mountain range respectively and finally at the east the valley prevails upon sea. This landscape and the valid evidence~~s~~ of its special geology~~;~~ was the reason for the first scientific studies that were conducted to the area. Over the recent years due to the increase of the standard of living and the increased pressures upon the environmental resources, the consequence was the shift of the scientific studies to issues that affect and are affected by the modern society. The geological studies were succeeded by hydrologic and environmental studies. Furthermore the increased industrial capacity of the valley and the need for planning new infrastructures for unhindered economic activity fueled the publication of special studies for environmental issues such as pollution and floods.

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The importance of the riparian ecosystems of Sperchios is not represented proportionally to their present value. As we will notice in the results, the riparian forested areas of Greece are overlooked by the local researchers due to the insignificant occurrence of wetlands and water bodies in Greece, less than 2% of total area [1]; therefore few riparian ecosystems in Greece, and the past strategic management from the state over the last century [2]; draining wetlands and shallow lakes and channelizing rivers and streams with earth and concrete levees. Over the recent years the state altered its policy, shifting its plans and infrastructure constructions towards a more environmentally–friendly approach e.g. the reestablishment of Karla Lake, Thessaly and the construction of Egnatia Motorway [2, 3].

The aim of this research is to record the literature till now of the Sperchios River up to the present day (for the period 1950 – 2015), to show the ecological importance of riparian ecosystems, to identify problems.

2. RESEARCH AREA

2.1 Riparian vegetation

The majority of the vegetation consists of plane trees *Platanus orientalis* forming dense and gallery forest and they are registered as *Platanion orientalis* alliance, their reference code to Natura 2000 is 92C0 and according to Palaearctic habitats their code is 44.71.[4]. In detail, pure stands of *Platanus orientalis* cover 714,30 Ha and 249,28 Ha in mix with *Populus alba*, *Alnus glutinosa* and *Salix sp.* . On the understory in various mixes we found *Atriplex sp.* , *Lolium sp.* , *Scripus sp.* , *Plantago sp.* etc. [5]. Beside the riparian forests, reed beds are forming along the river bank succeeded, in the plains near the mouth of the river, by thickets of *Tamarix sp.*, *Paliurus spina-christi*, *Rubus sp.* , *Spartium junceum* , *Onobrychis sp.* and around of 1100 Ha of wet meadows and salt marshes consisted by *Juncus maritimus*, *Salicornia patula*, *Scripus sp.*, *Hordeum sp.* and *Limonium sp.* [6].

2.2 Fauna

The ecosystems of Sperchios host many species, the most important of which will be mentioned. From the insect group we found the strictly protected species of *Leptidia duponcheli*, *Pieris ergane* and *Charaxes jasius*. The under protection reptiles occurring in the area are *Coronella austriaca*,*Vipera ammodytes*, *Ablepharus kitaibelli*, *Lacerta trilineata*. The occurring under special protection status mammals and fishes of Sperchios are *Nyctalus lasiopterus*, *Nyctalus leisleri* and *Lutra lutra* (registered in Greece Red Data Book) and the fishes of *Phoxinellus stymphalicus minutus* and the endemic critical endangered *Pungitius hellenicus* [7, 8].

2.3 Water

As many rivers in Greece, Sperchios exhibit a very seasonal flow from winter high fluxes to very low water levels during summer months. The key feature of the river is its sediment yield that reaches high values. The aquifers that supplies several springs that contribute to Sperchios are supplied by fragmented of high porosity calciferous formations of Oiti, Kallidromo and Othris mountains [9].

2.4 Geology

The topography of the river vicinity is expressed in gentle gradient that is based on quaternary sediments, forming meanders and idle channels, surrounded by crop fields usually separate from the river with levees. The formed sedimentary strata are made from clays, sands, gravels and cobbles [10].

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2.5 Human activities

The agricultural sector rules the current status of the river; levees constrain the riparian areas in most of its length minimizing the floodplains of the river, agricultural drainage systems increase the leakage of agrochemicals and fertilizers to the river and eventually to Sperchios estuary. Effluents from industries and villages end in the river [7], the city of Lamia is operating a sewage treatment facility since 1994 and discharge in a Sperchios ditch (Germaniki Tafros) of Sperchios [11]. Also several weirs are built in Sperchios and its tributaries.

2.5 Problems

The major problems of Sperchios deriving from the human interference to the river; levees, untreated effluents from local olive mills, the ineffective operation of sewage treatment facilities, illegal landfills located near river, that receive from locals construction debris, agricultural by-products and wastes located near river [12, 13].

3. MATERIALS AND METHODS

To complete the study, an internet search was conducted, up today published literature on the river Sperhios. The publications were grouped according their means of publication and by their subject. In grouping according to the publication's type there were created eleven (11) different types:
1. journal international, 2. journal national, 3. books, 4. conference international, 5. conference national, 6. workshops (workshops), 7. PhD, 8. Master, 9. bachelor thesis (Graduate), 10 studies and 11. research report from research programs - technical reports and maps.

The publications included in our study, are products of scientific research and unjustifiable popularized articles were not taken into account, although their number is very large. Also In our study, Publications referring exclusive about the Maliakos Gulf were excluded, in contrast combined publications referring to Sperchios River and Maliakos Bay were included recorded.
our second criterion is the subject of the publications (7) categories: 1) riparian and aquatic vegetation - riparian forests 2) Hydrology - Hydrogeology - Pollution 3) ground - Look - geology 4) fauna 5) HISTORY - ARCHAEOLOGY - mythology 6) geothermal energy - sources and 7) protection - management - ecosystems.

For the processing of the data was used the SPSS statistical package, and for creation of the graphs we used the Excel.

4. RESULTS AND DISCUSSION

The records about the Sperchios River are referring to the last 65 years, from 1950 to 2015. We retrieved more than 160 publications, in fact 166 published articles. The results from their analysis are presented in the following chapter.

4.1 Publication's types

The results referring to publication types are given in Table 1 The largest share is allocated to international journals, 31 papers recorded or 18.7% percentage, followed by research report - technical report-maps with frequency 27 or 16.3% of total publications. Impressive is the fact that the total number of scientific papers in international and national magazines reaches 41 papers namely 23.5% of the published work for Sperchios. Publications in international and national conferences are hovering at the same share which is 35 articles or 21%. The great interest in Sperchios A significant number of theses THESIS and dissertations have been accomplished referring to Sperchios and its environment. The books issued for Sperchios reach the 14 or 8.4% of publications.

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Table 1. Publications for Sperchio river per publication type

Type of Publication	**number**	**%**
Journal International	31	18.7
Journal National	8	4.8
Book	14	8.4
Conference International	16	9.6
Conference national	19	11.4
Workshop	5	3.0
PhD	6	3.6
Master	14	8.4
Bachelor thesis	7	4.2
Studies	19	11.4
Research & technical report- maps	27	16.3
Total	166	100.0

4.2 Publications according to their research subject

The published studies for Sperchios river have been grouped according to scientific subject which is given at Table 2. It is evident from our results that the largest portion of the publications are focused on issues of Hydrology, Hydrogeology and pollution or quality of the river water with 69 similar surveys or 41.6 % of published research. Publications about environmental protection and management attain 35 papers or 21.1%, while much research has been done about soil science, geology and the riverbed with 22 papers or 13.3% of publications. Studies on the subjects of riparian vegetation and riparian forests materialized during the last decade with a total of 7 posts or 4.2% of them.

Table 2. Publications for the Sperchios river per SUBJECT RESEARCH

Subject of Publication	**number**	**%**
Riparian vegetation & forest	7	4.2
Hydrology- hydrogeology- pollution	69	41.6
Soil – Bank- Geology	22	13.3
Fauna	6	3.6
History – Archaeology-Mythology	11	6.6
Geothermic- Spings	16	9.6
Protection – Management-Ecosystems	35	21.1
Total	166	100.0

A thorough look shows that the most scientifically popular subject of the publications is Hydrology- hydrogeology- pollution, Hydrology- hydrogeology- pollution with 69 publications (41.6% of total), the shares in the means of the later publications are allocated according to the

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following percentages the 27.5% are in journals, the 17.4% in Conferences, 23.19% PhD & Masters and 14.5% are Research & technical report.

The second more frequent publications topic is the Protection and Management reaching a quarter of their total number. Out of these 35 publications, the 25.7% is in journals, the 22.9% in conferences, 5.5% PhD & Masters and 8.6% are Research & technical reports.

The scientific subject that is placed as the third most frequent topic is Soil-Bank-Ecology: Soil - Bank- Geology. From 22 posts journals and conferences are sharing the same percentage with 27.3 %, followed by Masters and PhD's share with 4.5% , and finally Research & technical report and Studies are sharing the same percentage with 18.2 % of the publications.

The publications referring to History-Archaeology- Mythology forms a cluster in the issued books with 45.5% of the total publications followed by conferences and journals with percentages 36.4% and 18.1% respectively.

Publications about Environmental issues that are focusing on environmental status and its contents such as its riparian vegetation and forests, were published during the last decade. The largest portion (43%) of them were published in journals followed by Conferences and studies and technical reports with 28% and 29% respectively.

4.3 Publications per decade

Table 3 shows the temporal distribution of posts per decade from 1950 until 2015. today. From Table 2 and the Figure 1 it appears that the greatest scientific interest were manifested in two decades, those of 2000 and 1990, with 48 and 39 posts respectively, reaching approximately 52.4%. During the last 25 years the 73.5% of the total publications were published. Especially in the last five years, new research Was published about the riparian forest and vegetation of Sperchios.

Table 1. Publications for Sperchios river per decade

Decade	number of Publication	%
1950-1959	3	1.8
1960-1969	5	3.0
1970-1979	15	9.0
1980-1989	21	12.7
1990-1999	39	23.5
2000-2009	48	28.9
2010-2015	35	21.1
Total	166	100.0

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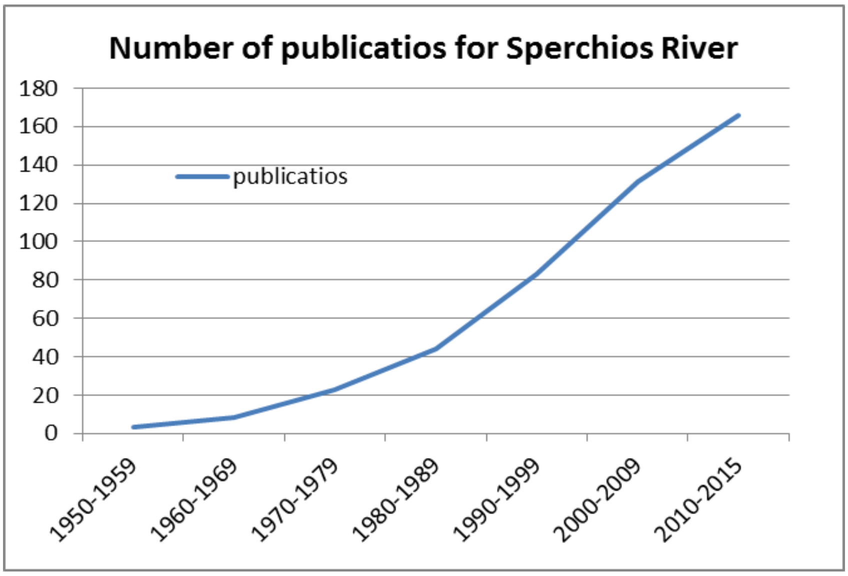


Figure 1. Evolution of publications for Sperchios river.

5. CONCLUSIONS

After the recording and analysis of the published work about Sperchios River, several interesting conclusions are inferred.

The scientific work which is published in international and national, journals and conferences, exceeds 44.5%, which indicates the importance of riparian ecosystems of Sperchios river.

The escalation of publications recorded in the ‘90s, In which the publications were almost doubled; compared to the previous decade sustaining its ascending trend in the following decades.

This is linked with the increased scientific interest of the scientific community about the riparian ecosystems as a result of the promotion, enhancement and public disclosure of the problems created in the river systems from the intense human activities in the basin, resulting in the awareness and the increased environmental concerns on behalf of citizens.

The importance of riparian ecosystems Sperchios is shown by the conception and delivery of theses and dissertations about the quality and the management of water resources in the river basin.

This trend was provoked by the serious and frequent floods of the river due to the anthropogenic interventions in Sperchios channel and its potential floodplains..

The topics of water quality, aquifer issues, geothermal and mineral springs, geology, hydrogeology and riverbed dominate the published work about Sperchios the last 65 years as recorded by our research. The flooding of the river is a matter of concern to the local community and the management authorities of the region.

Certainly the oldest publication ever recorded for Sperchios is a travel visit of Gordon M.G. in1838, at Thermopylae. Interesting is also another historical source for the region of Fthiotida which was published in 1973 and is actually a reissue of a historical book that was first published in 1907. From these reports it appears that the first publications of the last century for Sperchios related published work of historical and naturalist-travelers referred to the region of the river.

The publications for the riparian vegetation of the Sperchios river is quite recent and took place the last two decades. The first recorded reference About the riparian vegetation of Sperchios is a mapping made by NAGREF in 1991 and three years later in 1994 published by Koumpli-Sovantzi L. and Vallianatou I. [14], the first floristic scientific work for the region in a international journal. The first publication about the riparian forests of Sperchios was from the forester Gogoulos in 2004 [15], at the conference entitled "NATURA Sperchios-Maliakos": Interestingly, the first study about the plane-forest of Sperchios prepared by the forester A. Xyrogiannis, 2003 [16], director of Forest

Agency Department in Sperchiada. Especially in the last five years, new research published in the riparian forest and riparian vegetation of Sperchios. The publications for riparian vegetation and riparian forests have been up to 43% in peer-reviewed journals and 28% in scientific conferences, ie ¾ are scientific papers and the remaining approximately ¼ studies.

The increased number of publications about the environment highlights the distinctive features of the valley [17], and its delta as a legislated protection area, and also the problems and degradation that is facing due to anthropogenic impacts on the broader river basin.

References

[1] http://www.eea.europa.eu/soer/countries/gr/land-use-national-responses-greece (accessed March 18, 2016)

[2] Dodouras, S., Liratzaki, E. and Papayiannis, Th. (editors) (2014), *Walking guide Lake Karla, Mediterranean Institute for Nature and Anthropos* (Med-INA), Athens, 28-30 (In Greek).

[3] http://www.egnatia.eu/page/default.asp?la=2&id=19 (accessed March 19, 2016).

[4] European Commission DG Environment, 2007, *Interpretation manual of European Union Habitats, Brussels*, Belgium.

[5] Xyrogiannis, A., 2003. Management Report of Sperchios Platanus orientalis forest. Forest Service of Sperchiada. Sperchiada.

[6] Efthimiou G., Mertzanis, A., Sapountzis, M., Zakynthinos, G. 2005. Anthropogenic effects on Spercheios river Delta - Actions for Protection, Restoration and Management of natural ecosystems. *Proceedings of the International Conference HELECO '05,* February 3-6, Athens, Greece, 1-10.

[7] K. Georghiou, A. Legakis (Supervisor), Natura 2000 standard data form for site GR2440002, *the Ministry for the Environment, Physical Planning and Public Works (ΥΠΕΧΩΔΕ) and the Greek Biotope/ Wetland Centre (EKBY).*

[8] http://www.iucnredlist.org/details/18875/0. (accessed March 19, 2016).

[9] Daoulas E., 1995, "Flood infrastructure at Sperchios river ", *Proccedings "Sperchios 2000 + Environment and Development"*, Lamia 4th of May, 153-162 (In Greek).

[10] Maroukian H., Pavlopoulos K., 1995, Geology and Geomorphology of the river Sperchios drainage basin, Proceedings of *Proccedings "Sperchios 2000 + Environment and Development",* Lamia 4th of May, 203-215 (In Greek).

[11] http://www.lamia.gr/el/content/biologikos-katharismos (In Greek). (Accessed March 19, 2016).

[12] http://sperxeios.blogspot.gr/2009/06/blog-post.html. (In Greek). (Accessed March 19, 2016)

[13] http://sperxeios.com (Accessed March 10, 2016)

[14] Koumpli-Sovantzi, L.,Vallianatou I., 1994. Floristic notes from aquatic stands of Central Greece (Sterea Ellas), Candollea 49

[15] Gogoulos 2004. The riparian forests of Sperchios. *Proceedings of the national Conference on NATURA "Sperchios-Maliakos"*

[16] Xyrogiannis, G., 2003.Διαχειριστική έκθεση του platanus forest of Sperchios river. Forest Services of Sperchiada. Sperchiada.

[17] Topaloglou, C., Efthimiou, G., Perakis, C. 2014. Image classification with SVM in a NATURA 2000 network protected area in Central Greece. *Proceedings of the 1st International Geomatics Applications Conference "GEOMAPPLICA"* University of Thessaly, Greece, 8-11 September, 2014, Skiathos island, Greece, 307-313.

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Agroforestry for High Value Tree Systems: system description

A. Pantera[1*], P. J. Burgess[2], R. Mosquera Losada[3], G. Moreno[4], N. Corroyer[5], J. Mc Adam[6], A. Rosati[7], A. M. Papadopoulos[1], A. Graves[2], A. Rigueiro Rodríguez[3], N. Ferreiro-Domínguez[3], J. L. Fernández Lorenzo[3], M. P. González-Hernández[3], V. P. Papanastasis[8], K. Mantzanas[8], M. Upson[2], P. Van Lerberghe[9], N. Malignierand[10]

[1] Forestry and Natural Environment Management, TEI Stereas Elladas, Karpenissi, Greece.
[2] Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK.
[3] Department of Crop Production, EPS. University of Santiago de Compostela. University Campus, 27002-Lugo, Spain.
[4] Forest Research Group (INDEHESA). University of Extremadura. Plasencia 10600, Spain.
[5] Chambre d'agriculture de Normandie , Chemin de la Bretèque, CS 30059, 76232 Bois Guillaume Cedex, France.
[6] Agri Food and Biosciences Institute, Newforge Lane, Belfast BT95PX, UK.
[7] Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, centro di ricerca per l'olivicoltura e l'industria olearia (CRA – OLI), via Nursina 2, 06049 Spoleto (PG), Italy.
[8] Aristotle University of Thessaloniki, Department of Forestry & Natural Environment,Thessaloniki, Greece.
[9] Institut pour le Développement Forestier, France.
[10] Association Française d'Agroforesterie, France.
* Corresponding author: Email: panteranatasa@gmail.com

Abstract

This paper attempts to synthesize the agroforestry systems involving high value trees based on the information gathered under the framework of the FP7 research project "AGFORWARD". Although ecological and socioeconomical contexts vary among sites, these systems share some common challenges. The systems described involve apple, orange, chestnut, walnut and olive trees that are combined with agricultural crops such as chickpeas, barley and others or are grazed by sheep. In England, the grazing of apple orchards has long been a common practice and it is still practised on a considerable proportion of traditional orchards. The introduction of sheep to the orchard can minimize the need for mowing and at the same time it can positively contribute to providing animal feed for sheep production enterprises. In North-western France, pollarding is still a living practice very linked to the management of a typical landscape, where "bocage" ("traditional" hedgerows network on field boundaries) constitute the main component. In the South, pollards are generally found as remnants of a formerly much more widespread practice. In this wood-pasture, the land with trees is systematically grazed by domestic animals. In Spain, hardwood species are commonly harvested after long rotations of up to 50 or 60 years. Silvopastoral management and implementation of legume pastures could allow reducing the economic costs of these plantations and optimize their environmental functions. Agroforestry with chestnut (*Castanaea sativa* Miller) is a traditional land use system in North West Spain. Although chestnut groves are rarely intercropped (due to the low understorey production) or grazed (due to the fear of tree damage), the groves create a fine-grained mosaic of land uses including cropland and forests. Chestnut woodlands are also one of the best habitats for the commercial production of edible mushrooms. Another valuable system involves orange trees intercropped with chickpeas. Greece is the 17th of the 121 orange producing countries contributing 805500 tonnes to the world total of 71305973 tonnes. Finally, olive trees alone or in orchards are found in all parts of the country that have a mild Mediterranean climate. Olive trees are the only tree component in the typical olive culture. Quite often, however, other trees are found as well, including carobs (mainly in Crete), almonds, walnuts, apricots, fig, poplars, plums etc. (almost everywhere), either together with the olive trees or along the boundaries of the olive orchards. Animals may graze spontaneous vegetation or planted crops (ex. wheat or barley).

Keywords: apple; orange; olive; chestnuts; walnuts; grazing

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1. INTRODUCTION

Agroforestry is the practice of deliberately integrating woody vegetation (trees or shrubs) with crops and/or animal systems to benefit from the resulting ecological and economic interactions. Existing research indicates that appropriate application of agroforestry principles and practices is a key means by which the European Union might achieve more sustainable methods of food and fibre production whilst producing both profits for farmers and environmental benefits for society. The AGFORWARD research project (January 2014-December 2017), funded by the European Commission, is promoting agroforestry practices in Europe that will advance sustainable rural development.

Within the framework of AGFORWARD ten stakeholders groups were created across different countries in Europe to promote agroforestry involving "high value trees" such as fruit trees (e.g. olive [1, 2, 3], walnut [4], chestnut [5], apple [6, 7, 8], orange [9]) and trees grown for high value timber (e.g. walnut and wild cherry [10]). Stakeholders groups held national meetings between May and November 2014 to identify the main opportunities and challenges faced by this type of agroforestry in their farms. This Participative Research and Development Network (PRDN) is integrated in work-package 3 of the AGFORWARD project (http://www.agforward.eu/index.php /en/high-value-tree-systems.html).

Den Herder *et al* [11, 12] reported that agroforestry involving fruit, olive and nut trees covers about 2.7 million hectares, corresponding to about 0.6% of the territorial area in the EU. The area of agroforestry including other "high value" trees would therefore be higher. According to the same authors, the largest extent of agroforestry with high value trees can be found in Italy, followed by Greece, Spain, France, Portugal and Romania.

This paper provides a synthesis of ten "high value tree" agroforestry systems examined in the AGFORWARD projectwork-package 3 (WP3) based on their components, structure, ecosystem services and economic value. It includes each of the six countries listed above except Portugal and Romania.

2. COMPONENTS OF SELECTED SYSTEMS

In agroforestry systems there are three potential sets of elements that can be managed by humans; these are the tree or woody component, the herbaceous vegetation such as agricultural crops or forage pasture species, and livestock. As stated by Nair [13], in order for a land use system to be designated as an agroforestry system it should have a woody component. The tree component in the ten studied agroforestry systems were apple trees (3 systems), olives trees (3 systems) and chestnut, walnut, orange and ash trees (in the remaining four systems). It should be noted that ash (*Fraxinus* sp.) is included here due to its high timber value as well as its use as a forage tree. Mosquera *et al*. [14] found that the tree component has a major effect on understory production as it affects the amount of light reaching the ground. They state therefore that the trees most suitable for agroforestry will be those species that have low branch density and are self-pruning. The initial research suggests that there is a wide range of tree heights with the most intensive systems having a low canopy height of 2 m and the traditional systems reaching 12 m in height.

The potential choice of understorey crop species is particularly large in Mediterranean areas and can include cereals and horticultural crops such as asparagus, bulbs, mushrooms, grapes and wild grown species. Grass, with or without legumes, is the predominant understorey crop in most systems. It tends to be the dominant choice of understorey crop in Atlantic and Continental agroclimatic zones where radiation levels tend to be low. Grass is better adapted to shading than many arable crops because the focus is on vegetative growth and because the high biodiversity it has [15].

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Most of the silvopastoral systems with high value trees include sheep grazing on a grass component. One exception in Galicia in Spain is the use of an authochtonous pig breed as the animal component in an extensive system of chestnut. Because the primary focus in most high value tree systems is the tree component, it is important that the chosen animal species or breed will have to have only minor effects on the trees. Indeed, the choice of animal species and breeds that have only minor effect on trees is one of the main goals of most of the research groups participating in this project [16]. This is evident from the generally low stock densities used in most of these systems.

3. STRUCTURE OF SELECTED SYSTEMS

Most of the systems are composed of two strata which are vertically arranged in space. This spatial arrangement is common within the European agroforestry practices, as compared to the multi-strata systems such as the oasis systems found in North Africa or those related to home-gardens. Light or radiation constraints imposed by the high tree density on the crop component determine the type of plant species to establish. Two of the studied systems in the WP3 use shade tolerant species such as asparagus and mushrooms. This practice is of great interest to estimate their potential in other areas with market demand for these products, which may enhance farmers' income.

With the exception of the traditional olive, chestnut and pollarded systems, where trees are more scattered, trees are planted in linear rows. These linear systems are mostly intensive and/or modern systems with tree planted at high density in lines in order to facilitate the use of machinery. Tree density is lower in traditional and old, rather than intensive and relatively young systems, which allows farmers to reduce labour costs and increase production, and was identified during stakeholder meetings as one of the innovations that should be examined during the AGROWARD project [16].

In terms of the temporal arrangement, the systems can be characterized as coincident (grazed walnuts), intermittent (livestock grazing) and concomitant (all other systems). In many silvopastoral systems, sheep are removed during winter months due to scarce feeding resources, with the exception of the walnut systems in Spain. In addition, in the agrosilvopastoral olive system in Molos, Greece, sheep are introduced after the crop component is harvested. Each of the studied systems would appear to allow continuous long-term production, in that they use the same crop and animal components over time in a repeating annual cycle.

4. ECOSYSTEM SERVICES OF SELECTED SYSTEMS

Where measurements were taken, each of the agroforestry systems provided a range of ecosystem services, enhanced biodiversity, and help protect important habitats. Agroforestry provides numerous provisioning, regulating, cultural and supporting ecosystems services. A common characteristic of almost all the systems provide is that they food from both crops (olives, apples, nuts, vegetables) which is the main aim of the system, and animals (meat and dairy products). The only exception is the French pollard system that provides food as a livestock product (meat and cheese). Fuelwood is also a potential product from all the systems, and this should be promoted within the bioeconomy sustainable concept. In the case of olive trees, the wood is also used for local crafts and the production of various artefacts.

Agroforestry provides regulating ecosystem services such as local climate regulation. This is valuable, especially in Mediterranean areas where trees provide shelter to livestock and reduce the ambient high temperatures during the summer months and make them more resilient to extreme

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heat and temperature. Water quality improvement, nutrient cycling, and water flow regulation can also be important at a regional scale. Increased levels of carbon sequestration, stored in the above- and below-ground biomass of the trees, also contribute to global climate mitigation. Other regulating services include disease regulation and pest control, both issues of concern to the stakeholders that participated in meetings organised for AGFORWARD [16].

Agroforestry with high value trees also provides a variety of cultural and supporting services. These include improved aesthetics, increased employment and education opportunities, and maintenance of cultural heritage. As Isted [17] mentions, traditional agroforestry systems are an important part of the culture and heritage of many European areas, and in such areas they are viewed as systems that need to be preserved and sustainably managed.

5. ECONOMIC VALUE OF SELECTED SYSTEMS

As reported by Graves et al. [18], agroforestry systems and practices need to be financially viable and socially acceptable to practitioners. In this study all of the systems were commercially managed, with the exception of one subsistence system. Depending on the intensity of the system (traditional vs intensive) labour can be low or high. This is also related to the mechanisation level, which, in most systems, is high. High mechanisation levels can allow for more efficient management and can lead to higher economic return to the farmer. One of the significant inputs in many agroforestry systems is the labour of the individual farmer; however the perceived “cost” of labour varies between countries and farms. It is possible that some farmers do not see time spent on the farm as a cost but view it as a livelihood strategy or a way of life, and this has implications for the sustainability of such systems.

6. CONCLUSIONS

The primary focus of most “high value tree” agroforestry is the sustainable production of the high value tree species. However in many situations there are opportunities to integrate additional understorey crops or grass and livestock systems with either financial (related to the extra products provided, or the reduced management required for mechanical operations) or societal benefits (such as improved carbon sequestration for climate regulation, reduced water pollution, or improved aesthetic benefits of the landscape). These systems, most with a traditional base, provide a promising land management option which should be to be promoted.

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References

[1] Pantera A 2014a. Initial Stakeholder Meeting Report: Intercropping of olive groves in Greece (Kassandreia). 20 October 2014. 8 pp. Available online: http://www.agforward.eu/index.php/en/ intercropping-of-olive-groves-in-greece.html

[2] Pantera A. 2014b. Initial Stakeholder Meeting Report: Intercropping of olive groves in Greece (Molos). 20 October 2014. 9 pp. Available online: http://www.agforward.eu/index.php/en/intercropping-of-olive-groves-in-greece.html

[3] Rosati A. 2014. Initial Stakeholder Meeting Report Intercropping and grazing of olive orchards in Italy. 6 August 2014. 7 pp. Available online: http://www.agforward.eu/index.php/en/intercropping-and-grazing-of-olive-orchards-in-italy.html

[4] Pantera A. 2014c. Initial Stakeholder Meeting Report: Intercropping of Walnut Trees in Greece. 20 October 2014. 8 pp. Available online: http://www.agforward.eu/index.php/en/intercropping-of-walnut-trees-in-greece.html

[5] Mosquera Losada R, Ferreiro-Domínguez N, Fernández Lorenzo JL, González-Hernández P, Rigueiro Rodríguez A. 2014. Initial Stakeholder Meeting Report: Chestnut agroforestry in Galicia, Spain. 23 September 2014. 9 pp. Available online: http://www.agforward.eu/index.php/en/chestnut-agroforestry-in-galicia-spain.html

[6] Burgess PJ. 2014. Initial Stakeholder Meeting Report: Grazed Orchards in the UK. 18 July 2014. 8 pp. Available online: http://www.agforward.eu/index.php/en/Grazed_Orchards.html

[7] Corroyer N. 2014. Initial Stakeholder Meeting Report: Grazed Orchards in France. 1 December 2014. 8 pp. Available online: http://www.agforward.eu/index.php/en/grazed-orchards-in-france.html

[8] McAdam J. 2014. Initial Stakeholder Meeting Report: Grazed orchards in Northern Ireland, UK. 4 December 2014. 9 pp. Available online: http://www.agforward.eu/index.php/en/grazed-orchards-in-northern-ireland-uk.html

[9] Pantera A. 2014d. Initial Stakeholder Meeting Report Intercropping of Orange Groves in Greece. 18 November 2014. 7 pp. Available online: http://www.agforward.eu/index.php/en/intercropping-of-orange-groves-in-greece.html

[10] Moreno G. 2014. Initial Stakeholder Meeting Report Grazing and intercropping of plantation trees in Spain. 17 September 2014. 12 pp. Available online: http://www.agforward.eu/index.php/en/grazing-and-intercropping-of-plantation-trees-in-spain.html

[11] Den Herder, Michael den Herder, Paul Burgess, María Rosa Mosquera-Losada, Felix Herzog, Tibor Hartel, Matthew Upson, Iida Viholainen and Adolfo Rosati. 2015. *Preliminary stratification and quantification of agroforestry according to systems studied in WP2-WP5*. Available online: http://www.agforward.eu/index.php/en/preliminary-stratification-and-quantification-of-agroforestry-in-europe.html?file=files/agforward/documents/M1_Stratification%20of%20agroforestry.pdf

[12] Den Herder, M, Moreno G, Mosquera-Losada R, Palma J, Sidiropoulou A, Santiago Freijanes JJ, Crous-Duran J, Paulo J, Tomé M, Pantera A, Papanastasis V, Mantzanas K, Pachana P, and Burgess PJ. 2015. *Current extent and trends of agroforestry in the EU27*. 4 December 2015. Available online: http://www.agforward.eu/index.php/en/current-extent-and-trends-of-agroforestry-in-the-eu27.html?file=files/agforward/documents/D1_2_Extent_of_Agroforestry.pdf

[13] Nair, PKR. 1985. Classification of agroforestry systems. *Agroforestry Systems* **3**: 97-128

[14] Mosquera Losada R, J.H. McAdam, R. Romero-Franco, J.J. Santiago-Freijanes and Rigueiro Rodríguez A. 2009. Definitions and components of agroforestry practices in Europe. In Book: *Agroforestry in Europe: Current status and future prospects*. Springer Science.

[15] Pardini a, Mori S, Rigueiro-Rodríguez A, Mosquera-Losada MR. 2010. Efecto del arbolado en la producción de pasto y trigo (" Triticum aestivum" L.) ecológicos en la maremma toscana (Italia central). *Pastos*: **40(2):**211-223

[16] Pantera A, Burgess P J, Corroyer N, Ferreiro-Domínguez N, Fernández Lorenzo J L, González-Hernández P, Graves A, McAdam J, Moreno G, Mosquera Losada R, Rigueiro Rodríguez A, Rosati A, and Upson M. 2015. *Report on Innovations to be examined for Agroforestry for High value Tree Systems*. Available online: http://www.agforward.eu/index.php/en/agroforestry-innovations-to-be-exam-ined-for-high-value-tree-systems.html?file=files/agforward/documents/Milestone3_2_Innovations.pdf

[17] Isted R. 2005. Wood pasture and parkland; overlooked jewels of the English countryside. In: Mosquesa-Losada MR, McAdam J, Rigueiro-Rodríguez A (eds.) *Silvopastoralism and Sustainable Land Management*. CABI, Wallingford, UK

[18] Graves AR, Burgess PJ, Palma JHN, Herzog F, Moreno G, Bertomeu M, Dupraz C, Liagre F, Keesman K, van der Werf W, Koeffeman de Nooy A, van den Briel JP. 2007. Development and application of bio-economic modelling to compare silvoarable, arable and forestry systems in three European countries. *Ecological Engineering* **29**: 434-449.

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Technical works for the environmental management of the Agia Lake in the prefecture of Chania, Crete

K. Papamanolis

Department of Civil Engineering, Faculty of Engineering Aristotle University of Thessaloniki, Greece.
Email: kostpapama@yahoo.gr

Abstract

The Agia Lake is a small artificial Lake in the Prefecture of Chania, Crete. It is used as a recreation area and, at the same time, is used to irrigate agricultural land in the region. The Lake is now a habitat for many species of flora and fauna and is included in the Natura network. One of the problems of the Lake is the drop of its water level during the summer due to the over-extraction of its water. This problem occurs increasingly in recent years and especially during the years with reduced rainfall. The work presents the technical works and actions that have as their primary objective the control of the level and the quality of the waters of the Lake in order to protect it effectively.

Keywords: Agia Lake; environmental management; reservoir; wetland

1. INTRODUCTION

The Agia Lake is located near the village of Agia (after which it was named), in the Prefecture of Chania, in Crete, approximately 9 km from the city of Chania. It covers an area of approximately 30 ha, it is located at an altitude of 80 m and is about 5 km from the Sea (Figure 1). The Agia Lake is artificial. It was created in 1927-28 in the catchment of Keriti, with the construction of a dam which interrupts the flow of a tributary of Keritis, the Xekolomenos. The water of the Lake is supplied from the tributary and from springs located on its banks and its bottom. The area was a marsh before the Greek Public Power Corporation (PPC) turn it into an artificial Lake, for the production of hydropower via a power plant. Now, the power plant of PPC doesn't operate.



Figure 1. Panoramic view of the Agia Lake.

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This small Lake hosts a wide variety of aquatic plants, but also very important species of fauna, including rare species of fern and frogs. The Lake is also a natural shelter for many birds, migratory or not. It is characteristic that it hosts around 215 species of aquatic and predatory birds. The ecological significance of the Agia Lake is reflected on the fact that it is included in the Natura 2000 network and is protected by international treaties. However, this important ecosystem is threatened by three main categories of problems:

1. Pollution of groundwater and surface waters in several cases is caused by the misuse of pesticides, chemical fertilizers, waste etc. Part of the pollution comes from nutritious ingredients and contaminants from upstream of the tributary that empties into it as he passes by farms and residential areas without sewers. Furthermore, the area around the basin of the Lake is covered by farmlands, especially with citrus crops.
2. The over-exploitation of water. The problem is most acute in the summer due to flawed agricultural practices, such as watering at times of great heat (which is harmful for plants too) or replace traditional crops (e.g. the xerophyte olive) with others that require a lot of water. Also, the fact that in recent years the waters of the Lake are pumped for water supply needs of neighboring areas and other activities, led to the deterioration of the problem.
3. The solid waste deposits, the earth fillings, the land clearings, the plotting and building and other unauthorized activities on the banks. A part of these effects is connected with the use of the Lake as a recreation site.

To tackle the problems that the Lake faces, administrative and technical measures have been taken occasionally. The first include verification of the quantity and quality of the water of the Lake and executive measures for their preservation at satisfactory levels. The technical measures regard works and actions for reducing water losses and increasing capacity of the basin.

This work describes the technical works and action that have been implemented (and programmed) aiming at environmental management and utilization of Agia Lake and its surrounding area.

2. THE ARTIFICIAL AGIA LAKE

The artificial Agia Lake became operational in 1929 for the support of the Small Hydroelectric Plant (SHEP) Agia of PPC, one of the first hydroelectric plants in Greece. The SHEP, at its launch, had a total power of 0.90 MW, with three units of 300 KW each.

The total area of the Agia Lake, at its highest level, is estimated at 120,325 m^2 and its volume at 215,138 m^3. Concerning the depth of its waters, maximum depths ranging from 4 to 7 m at the time of its creation are reported. Nevertheless, the Lake depth fluctuates, mainly with seasonal variation, as follows:

Spring: The Lake is filled with water. Statistically, the maximum water level is reached at early spring.

Summer: The Lake level drops because its waters are used for irrigation and water supply. Some years it dries completely with result goats to graze on its bottom. Other years it maintains water in streams and puddles at its bottom (Figure 2).

Autumn: Begins to fill again with water.

Winter: Continues to fill with water. In episodes of intense rainfall, overflows that cause damage to the surrounding area are often observed.

The average supply of water in the Lake is estimated to be approximately 7885 m^3/h. This implies that in the Lake flow in (and, correspondingly, flow out) approximately 69 million m^3 per year.

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Figure 2. The Agia Lake dry (August 2014).

The Lake, since its creation, gradually acquired wetland characteristics. These characteristics retained after the operation of the hydroelectric power plant stopped (two of the three units were decommissioned in 1968 and the last one in 2009). On May 23, 2009, the Lake, along with the other facilities of the power station, were granted from the PPC Renewable Energy, a subsidiary of the PPC, to the Chania Prefecture, "in order to create a green space and recreation area and in this way to contribute significantly to the environmental upgrading in the region".

The area of Agia Lake is registered as a wetland in the Greek Wetlands Inventory of the Greek Biotope/Wetland Centre (EKBY) with the following information[1]:

AGIA RESERVOIR

- **Wetland Code: 434376000**
- **Geographical Coordinates:** Longitude: 23°55'00" Latitude: 35°29'00"
- **Location:** 1 km SW of the Agia village.
- **Altitude above sea level (m):** 80
- **Area (ha):** 7
- **Wetland Type:** Reservoir (predominant type)
- **Biotic characteristics:**
- **Flora:** Emergents: *Typha domingensis, Scirpus maritimus, Schoenoplectus tabermontani*
- **Fauna:** Birds: *Hieraaetus fasciatus* (vulnerable), *Circus aeruginosus* (vulnerable, migratory)
- **Most significant present values:** Irrigation water (great), Game support (great), Scientific (medium), Recreational (medium), Educational (medium)
- **Significant present uses:** Irrigation water supply (high), Hunting (low)
- **Factors changing the wetland's ecological character:**
- **Pollution:** Municipal wastewater (great), Municipal solid wastes (great), Agricultural point source pollution (medium), Non-point source agricultural pollution (great)
- **Other anthropogenic activities:** Establishment of new housing facilities or expansion of old ones (small), Overpumping of ground water (great), Irrigation schemes (great), Establishment or expansion of cultivated fields (small), Establishment or expansion of livestock facilities (small)
- **Most significant positive actions:** Ecological studies

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Now, the area of the Agia Lake has highly developed flora and fauna and offers shelter to rare species of birds, fishes and amphibians. For this reason, it has been included in the Natura 2000 Network and has been designated as a Site of Community Importance (SCI) under Directive 92/43/EOK, codenamed GR4340006, and as a Special Protection Area (SPA) under Directive 79/409/EOK, codenamed GR4340020 [2,3].

3. THE PRESENT SITUATION

The Lake of Agia, particularly during the last two decades, has received strong environmental pressure with significant impact in its qualitative and quantitative characteristics and the ecosystems which it hosts. The bulk of this pressure is man-made and includes:

a. Activities that cause pollution of waters, as pollution from farm work and disposal of solid waste and rubble.

b. Disturbing activities near the Lake, as recreation, hunting etc.

c. Exploitation of its waters.

A recent study of physico-chemical parameters of the water of the Lake showed that, based on the classification system of the WFD Common Implementation Strategy [4], this is in the "High" condition regarding the values of hydrogen ions (pH) and total Nitrogen (TN) and in the "Bad" condition regarding the values of total Phosphorus (TP) measured [5]. Similar studies have highlighted the problem of pollution of the waters of the Lake as a result of agricultural activity in the region (in the area operates a farm, while in the basin of the Lake there are systematic citrus crops) and the proximity of built-up areas without sewers [6]. A phenomenon associated with the pollution is the expanding of the vegetation (especially of Reedy) inside the Lake, with negative effects on its ecosystems.

The over-exploitation of the waters is a serious environmental problem for the Lake. The waters of the Lake are being exploited for different uses from 5 local agencies: The Land Reclamation Organization of Varipetro, The Municipal Enterprise for Water and Sewage of Chania, The PPC, The Organization for the Development of West Crete and The Land Reclamation Organization of Agia-Kolymbari. Still, illegal water abstractions from individuals have been denounced. As a result of increased pumping for meeting the needs in irrigation and water supply, there have been several cases where the Lake has completely lost its waters. Especially during the summer season in recent years, it is quite often for the Lake to turn into a shallow swamp. The problem is most acute in years marked with smaller rainfall, as it was for example in 2012 and 2014. It is also characteristic that the depth limit of 1.4 m which, in recent years, has been nominated as a measure for the protection of Lake ecosystems, often, is being trampled.

The drop in water level of the Lake is also linked to the reduction of its capacity due to earth fillings and accumulation of sediment on its bottom. In fact, because of these problems, it is estimated that, the capacity of the reservoir was restricted to approximately 50,000 m^3 [7].

4. WORKS AND ACTIONS FOR ADDRESSING THE PROBLEMS

It is widely accepted that the large part of the problems facing the Agia Lake is due to the lack of coordination among the agencies involved in its management and exploitation [8]. Accordingly, a decision has been taken by the Region of Crete for the elaboration of an integrated Special Environmental Study that will provide for the establishment of a management body of the Lake and the surrounding area as an important step for the rational management and protection of this important wetland [9].

A series of works have been launched for the operation of the Agia Lake as a model environmental Park. These works include:

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- Appropriate delineation of the area of the Park to make the maintenance of the site feasible and effective.
- Re-planning and delineation of the paths for pedestrians and bicycles on the West, North and South zone (Figure 3).
- Creation of resting points at regular intervals and in appropriate places with good visual contact with the natural beauty of the Lake. These points will be equipped with appropriate shelters or observatories of the natural environment and the bird life.
- Creation of a central point of entry with appropriate information and marking.
- Organization of a car parking area.
- Organization and enrichment of the planting.
- Planning and organization of the necessary urban equipment (observation points, shelters, information kiosks, toilets, resting points, waste bins, informative signs, traffic barriers, lightings and constructions and games for the younger visitors).
- Renovation of the premises of the old hydroelectric plant and its conversion into a Renewable Energy Museum and environmental education center (Figure 4).



Figure 3. A new pavement at the periphery of the Agia Lake.



Figure 4. The renovated building of the old hydroelectric plant.

These works, many of which are already being executed, are mainly located in the Western zone of the Lake, where is the main entrance, while retaining the eastern zone untouched as there are the most sensitive components of the ecosystem of the Lake.

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Recently, bathymetry and mapping of the vegetation in the Agia Lake was conducted aiming to study the accumulation of sediment on its bottom [10]. As a follow-up to this study, a new study was conducted to clean the bottom of the Lake and increase its capacity. The dredging is planned to become gradually on parts of the bottom to protect the biodiversity of the Lake [11].

Also, in the region, infrastructure projects are executed and studied that will have an indirect effect on the environmental protection of the Lake, like:

- New boreholes to cover part of irrigation and water supply needs that are now covered by the waters of Lake [8].
- Maintenance works on the water transmission network from the Lake, for mitigation of losses.
- Sewerage system in residential areas in the drainage basin where the Lake belongs [12].

5. CONCLUSIONS

The Agia Lake is a good example of an artificial lake that is no longer used for the purpose for which it was constructed, i.e. to support a hydroelectric plant, but has evolved into an important habitat and recreation place. Nevertheless, while the Agia Lake is a very important ecosystem of Crete, is facing man-made impacts that threaten its environmental characteristics like other ecosystems near inhabited areas. The most important of these impacts infers to the pollution and the reduction in water levels due to the over-exploitation, mainly during the summer season.

Dealing with the effects and the preservation of the ecosystem of the Lake is attempted with a series of works and actions in the region. These works and actions cover different aspects. The most important of these concern the limitation of pollution of waters, the control of the water level of the Lake and the convenience of visits to the site without disturbing the ecosystems of the Lake. Some of the works have been executed and already have a positive impact in the region. Others are in the process of implementation or programming. The completion of these projects is estimated to contribute to effective environmental management and protection of the area for the benefit of society.

References

[1] Zalidis, G.C., Mantzavelas, A.L. (Eds), 1995. Inventory of Greek Wetlands as Natural Resources, The Goulandris Natural History Museum, Greek Biotope/Wetland Centre (EKBY), p. 475

[2] http://www.ypeka.gr/LinkClick.aspx?fileticket=3xSIBliyZME%3D&tabid=251&... (accessed April 20, 2016).

[3] http://www.ecovalue-crete.eu/el/sites/gr4340006 (accessed April 20, 2016).

[4] European Commission, 2003, Common Implementation Strategy for the Water Framework Directive (2000/60/EC).

[5] Prountzos, S.S., 2013. Identification of water bodies in Western Crete based on the Water Framework Directive 2000/60/EC, School of Rural and Surveying Engineering, National Technical University of Athens, p. 234.

[6] Stavroulakis, G., Kakoulaki, G., Papafilipaki, A., Kiriou, M. 2007. Study of the polluting load of Agia Lake. *Proceedings of the 13th Pan-Hellenic Conference of Ichthyologists*. Quality Control Laboratory of Water and Soil Resources, TEI of Crete, Chania.

[7] http://www.haniotika-nea.gr/vithometrisi-ke-chartografisi-vlastisis-stin-limnis-tis-agias/#ixzz45mTqzMnD (accessed April 20, 2016).

[8] Agorastaki, G., 2002. Water Reservoir Management in Crete, *Presentation in the Workshop for "Artificial Wetlands and Lakes in Crete"*, MAICH, Chania.

[9] http://www.haniotika-nea.gr/katharismos-tou-vithou-sti-limni-tis-agias/ (accessed April 20, 2016).

[10] Natural History Museum of Crete, 2015. Study of the Problem of Accumulation of Sediment Deposits at the bottom of Agia Lake, p. 40.

[11] http://www.haniotika-nea.gr/miomenes-kata-30-50-i-vrochoptosis-sta-chania/ (accessed April 20, 2016).

[12] http://agonaskritis.gr/κοινή-συνέντευξη-τύπου-προέδρου-δευα/ (accessed April 20, 2016).

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Solid Waste Management

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Site and size selection methodology of Waste-to-Energy facilities targeting R1 maximization and gate fee minimization. A concrete approach.

E. G. Kyriakis[1], C. S. Psomopoulos[2,3*], P. I. Kokkotis[2], A. Bourtsalas[3], N. J. Themelis[3]

[1] Sch. of Eng. and Ph. Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK
[2] Department of Electrical Engineering, Piraeus University of Applied Sciences, 250, Thivon & P. Ralli Ave., 12244, Egaleo, Greece
[3] Earth Engineering Center, Columbia University, New York, U.S.A.
*Corresponding author: Email: cpsomop@teipir.gr

Abstract

A growing urban population along with a shift towards modern lifestyle, result in the production of large quantities of Municipal Solid Wastes (MSW). 80% of these wastes end in dumpsites, while the rest are laid in sanitary landfills.

This study focuses on the exploitation of the MSW generated and suggests an algorithm which can provide us with a step-by-step selection method for the location and the size of a Waste-to-Energy (WtE) facility targeting for the maximum energy output, while also considering the main obstacle, which, in many cases, is the final gate fee.

The developed algorithm has been validated with typical case studies in Greece.

This study's results reveal that the development of a solid approach in selecting the site and the size of a WtE facility can be feasible. However, the maximization of the R1 energy efficiency factor requires high utilization factors. The minimization of the final gate fee requires high R1 values and high amounts of metals' recovery from the bottom ash, along with an economic exploitation of recovered raw materials, if any.

Keywords: *R1 factor; Waste-to-Energy facility; municipal solid wastes management; gate fee minimization*

1. INTRODUCTION

As the population is growing in large urban centers as well as the shift to a modern consumer lifestyle, have resulted in the production of large quantities of municipal solid wastes [1]. The concentration of wastes is a major issue in such societies and their proper management is imperative and necessary. Unfortunately, only 20% of the existing landfills are sanitary [2] while a high percentage of the existing landfills are dumpsites. Wastes disposal on landfills is responsible for carbon dioxide (CO_2) and methane (CH_4) emissions, while the latter enhance the greenhouse effect 25 times more than carbon dioxide [3].

An alternative option in waste management can be the energy recovery or energy from wastes. Energy recovery from wastes can be achieved through two processes: Biological and thermo-chemical process. The first one includes anaerobic digestion as well as fermentation while the second includes combustion, pyrolysis and gasification [4]. However, the majority of waste to energy facilities are focused on thermal treatment technologies and particularly on combustion process [5]. MSW that cannot be recycled or landfilled can constitute a fuel in waste to energy facilities.

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It has been proven that wherever a waste to energy facility is operational, the recycling rates have increased, too [6]. Thus, we can say that WtE facilities can enhance the recycling rates instead of reducing them. Moreover, waste to energy facilities can reduce the weight and volume of municipal solid wastes by 75% and 90% respectively, avoiding land capture for sanitary landfills [7].

On the other hand, waste to energy facilities can produce energy in the form of electricity and heat. Energy from wastes, according to US Department of Energy, is recognized as a renewable source of energy in the form of biomass due to the large percent of included organic materials, in contrast with included materials derived from fossil sources. Nowadays, the development of renewable energy is high at the public agenda compared to other forms of energy, in order for the environment and the human health to be protected.

A major issue which emerges when a waste management system is going to be implemented is the land usage. Nowadays, as the population is growing, mostly in urban areas, reaching high density, land available for waste treatment method is obviously crucial. Furthermore, country islands with restrict boundaries have to face the same problem. It is known that landfilling methods require large available land area in order to be proper designed and operational and when a waste management system has to be considered in countries where lack of available land is a problem [5]. Waste to energy facilities could be an attractive solution for coping with such problems. Thus, land requirements for waste to energy plants are dramatically decreased and due to high pollution control and the possibility to support increased energy demands, in the form of electricity, heat and cooling, could be feasible for these facilities to even be implemented in the center of the town [5]. However, a crucial point that should be taken into consideration in the development process of energy recovery facilities is the gate fee. According to "Costs for Municipal Waste Management in the EU" European Commission report [8], the gate fee is defined as: "*The gate fee paid represents a unit (usually per tonne) payment made by the local authority to the service provider to generate a stream of revenue*". It is a cost that is usually covered by local authorities but also is depending on the administrative structure of each country. Sanitary landfills have cheaper gate fee than energy recovery facilities [5], therefore, the latter in order to be more attractive must adopt techniques that could reduce it to the minimum possible.

European Union, in an attempt to ensure the quality of energy production, introduced efficiency criteria specifically for the energy generated by MSW, in the energy sector at first. Thus, according to the Waste Framework Directive 2008/98/EU**,** an energy efficiency factor (R1 formula) has been established. This efficiency factor when has values over 0.60 leads to a combined waste treatment method and energy recovery facility otherwise the plant is characterized as disposal (D10) i.e. only waste treatment facility [9]. It is also an energy factor that is based on energy balance of the under study facility and express the output power utilized, also determining the corresponding size of the facility. Thus, R1 formula focuses more in the increase of the exploitation of energy derived used by third parties [10].

2. METHODOLOGY

The collected data that will be described in this chapter will be processed by using the developed Algorithm (Figure 2). The interaction between these data will reveal the most appropriate site and the size of the plant, when compared to other locations, where the energy factor is the highest and the gate fee is the minimum possible. The interaction of the data collected are targeted to evaluate a specific site, mainly according to the technical considerations of the proposed area. When the technical aspects of the area have been satisfied, each area is evaluated according to its potential in reaching maximum energy efficiency factor and minimum gate fee.

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2.1 Site evaluation model

The major advantage that WtE plants have is the small land requirement along with the major environmental benefits. However, various technical considerations have to be taken into consideration when a specific area is proposed for the implementation of such a facility. Below we summarize what technical parameters should be satisfied in order for an accurate evaluation to be as accurate as possible.

- Proximity to waste generation center
- Proximity to electricity connection lines
- Proximity to district heating or cooling
- Proximity to water
- Proximity to industrial steam consumers
- Proximity to landfill (for ash disposal)
- Proximity of fuel sources
- Access roads
- Traffic
- Utilities

2.2 Size evaluation model

The available solid wastes as feedstock in incineration plant with energy recovery, as it may be easily realized, constitute the ultimate parameter of WtE concept which also determines the size of the plant. Once the available amount of MSW ready to be treatment in incineration furnaces has been determined, the estimation of calorific value constitutes the major factor that may reveal their ability to produce sustainable and clean energy. It is the initial parameter which its estimation concludes to energy input of the system. Compounds with high NCV have resulted in high energy input and therefore increased power output.

However, what should be also emphasized is the potential of heat users. It is not common sense for a plant to produce a specific power output based on the available MSW where fewer users are ready to exploit this power. Incorrect dimensioning of the plant may result to loss of energy production while installation and operation cost would not be coped with. Consequently, the estimation of the available MSW that can be used for energy recovery must be properly studied and guaranteed through the year in order to ensure the feasibility of the plant. According to [11] an estimation of the installed capacity of the plant (Y) can be achieved by using the next equation 1, where X the amount of MSW:

$$\mathrm{Y} = 9 \cdot 10^{-5} \cdot X - 2.49 \qquad \text{(Eq. 1)}$$

Since there are several available technologies for thermal treatment of wastes including grate combustion, fluidized bed, RDF combustion, rotary kiln technology, as well as gasification processes such as pyrolysis and plasma, the most proven technology with wide range of implementations, is the grate combustion using MSW as received as feedstock, representing 80% of the installations worldwide. Consequently, in order to reach the most reliable results, the above mentioned technology has been selected. The energy recovery by using this technology is at the range of 0,5MWh – 0,7MWh per tonne of MSW when the plant's output is only power. In case of heat production, the energy recovery can be as high as 2MWh. When a CHP scheme is implemented the output of the plant can reach 0,5MWh – 0,6MWh electricity plus 1MWh heat.

The energy contained in MSW when combusted can be converted into useful energy in the form of electricity, heat and steam. Various WtE plants based on the potential market, they use the most appropriate technology to produce energy. Thus, globally, there are operational plants that their energy production is either in the form of electricity or heat as well as they use CHP technology in order to achieve both electricity and heat production. Energy Report III (status 2007-2010) issued by CEWEP (2012) reveals that across Europe there are in operation 184 WtE plants using CHP technology, 83 plants that only produce electricity and 47 plants that only produce heat. Accordingly, the mean energy recovery rate was 21.6% for plants only producing electricity, 77.2 for plants only producing heat, while the energy recovery rate for CHP plants was 15% for power and 37.5% for heat respectively.

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2.3 R1 energy factor estimation model

European Union, pioneering, has introduced an energy factor in order to ensure the quality of energy production. However, specific values of this factor must be reached for the authorization of the plant. Waste Framework Directive 2008/98/EU has set this value in the order of 0.60 for plants that were granted permit before December 2008 and 0.65 for future plants or plants that will be granted permit after the particular date.

The energy efficiency factor can be calculated from the following equation 2:

$$R_1 = \frac{E_p - \left(E_f + E_i\right)}{0.97 \cdot \left(E_w + E_f\right)} \quad \text{(Eq. 2)}$$

According to European Commission guidelines for the interpretation of the R1 energy efficiency formula for incineration facilities (2011), each indicator represents:

Ep means annual energy produced as heat or electricity. It is calculated with energy in the form of electricity being multiplied by 2.6 and heat produced for commercial use multiplied by 1.1 (GJ/year).

Ef means annual energy input to the system from fuels contributing to the production of steam (GJ/year).

Ew means annual energy contained in the treated waste calculated using the net calorific value of the waste (GJ/year).

Ei means annual energy imported excluding Ew and Ef (GJ/year).

0.97 is a factor accounting for energy losses due to bottom ash and radiation.

2.4 Economic analysis model

In order to formulate a comparative economic analysis, both expenses and revenues have to be investigated. The expenses of a WtE include the construction cost of the facility, the land cost for the implementation, the maintenance and operation cost, the cost of imported fuel as well as the transportation cost. Gains of a WtE facility include electricity, heat and steam revenues, credit carbons and metal recovery revenues and the most important, the revenues from gate fee.

Although the above mentioned revenues constitute a considerably economic support for the project, what should also be properly calculated is the gate fee. It is a cost that is usually covered by local authorities but also is dependable on the administrative structure of each country. Consequently, this gate fee represents the expenses for a proper waste treatment. Comparison of gate fee paid by the authorities between landfilling method and waste treatment with energy recovery reveals that the latest require by far higher gate fees. According to [1], a Waste-to-energy facility can be characterized as an attractive alternative option for waste treatment method when gate fee is considered low or government supported.The typical mathematical model used for the economic analysis, in order to estimate the economic feasibility of the project, is mostly based on the final determination of the gate fee. The evaluation of expenses and revenues of the plant, by using several economic tools such as NPV, the IRR and the CPBP, will finally formulate the corresponding gate fee for the proposed area and the size of the WtE facility.

3. RESULTS AND DISCUSSION

The collected data will be processed by using the next Algorithm (Figure 2). The interaction between data will reveal the most appropriate site and the size of the plant, when compared to other locations, where the energy factor is the highest and the gate fee is the minimum possible.

Since there are no WtE facilities in operation in Greece, the proposed country has been selected in order to validate the proposed algorithm. More specifically, four Greek cities such as Athens,

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Thessaloniki as well as Larisa and Volos have been selected due to increased population toward Greek cities resulting to increased amount of municipal solid wastes as well as due to high population density and therefore to the lack of available land area for implementation of a proper waste treatment method. Furthermore, a considerable number of industries are active in these regions resulting to higher utilization of the heat output. The amount of MSW produced in Greece according to [12] is almost 450kg per capita, which 39% is generated in the wide area of Attica, while 19% is generated in Central Macedonia where the city of Thessaloniki is situated. Two waste management systems in Greece are used: landfilling and composting. The first one treats the 88% of the generated MSW while composting is used for the rest 12% [13].

Athens is the biggest city in Greece and constitutes the capital of the country. However, the examination of the Athens city includes the wide region of Attica. The city is located in central Greece, it has an area of 3,808km^2 and cover 2.9% of the total area of the country. According to the last census (2011), the population of Attica was 3,752,973 [14]. Being the city with the higher population has resulted to high generation of MSW. Thus, the potential of wastes generated for treatment in a WtE plant is about 2200kt [15] annually with NCV about 9-10 MJ/kg.

Thessaloniki is the second biggest city in Greece after Athens and according to the last census (2011) the population was 1,104,460 [14]. However, the examination of the Thessaloniki city includes the wide region of Thessaloniki. It is located at the north of the country, covering an area of 3,683 km^2. It is also a city with high population and large amount of MSW are generated, reaching almost 971kt [15] per year with NCV about 9-10 MJ/kg.

In the region of Central Greece, two cities are going to be investigated. The cities of Larissa and Volos. The amount of MSW generated annually in Central Greece is about 632,000 tons [15]. According to technical considerations for the sitting of a plant, the two proposed cities present almost the same characteristics with small differences regarding population and industries. According to the last census, the population in Larisa was 144,651 while in Volos was 125,248. Furthermore, the number of active industries in Larissa is slightly more than in Volos. Therefore, the implementation of a WtE facility with annual capacity 200,000 tons is proposed.

In Figure 1, the energy production, with a NCV equal to 10MJ/Kg, in various forms based on the energy technology installed in each WtE plant, is illustrated. It is obvious that the energy production in the form of heat is by far greater than other technologies. Assuming that the annual heat demand per capita is equal to 2,500kWh$_{th}$, the heat production may cover almost 760,000 inhabitants by means of DH including a lot of municipalities near in the wide area of Athens [16]. In case of electricity production only, and assuming that the electricity consumption in Greece is 1500kWh per capita, the energy production can cover the electricity needs of about 355,000 inhabitants.

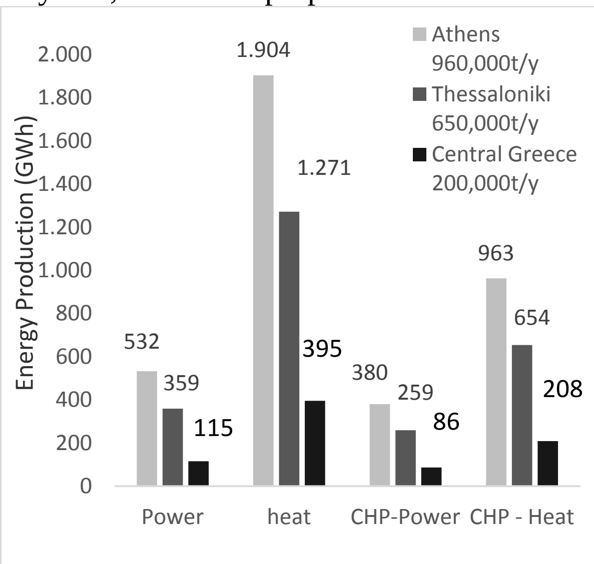


Figure 1. Energy Production of WtE plants.

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Table 1. Results of Energy Efficiency Factor (R1) based on Energy Recovery Rate and Utilization Factor

	Energy Efficiency Factor – R1			**Energy Recovery Rate (%)**			**Utilization Factor (%)**		
Site	*Electricity*	*Heat*	*CHP*	*Electricity*	*Heat*	*CHP*	*Electricity*	*Heat*	*CHP*
Athens (960,000t/y)	0.69	0.76	0.86	21	74	53	90	75	75-90
Thessaloniki (650,000t/y)	0.68	0.751	0.81	22	74	55	90	75	75-90
Central Greece (200,000t/y)	0.679	0.77	0.769	23	76	57	90	90	75-90

Table 2. Results of Gate fee and Size of the plant

	Electricity		**Heat**		**CHP**	
Site	*Gate fee (€)*	*Size (MW)*	*Gate fee (€)*	*Size (MW)*	*Gate fee (€)*	*Size (MW)*
Athens (960,000t/y)	58	74	54	265	48	187 (53+134)
Thessaloniki (650,000t/y)	63	50	58	177	52	127 (36+91)
Central Greece (200,000t/y)	102	16	101	55	95	41 (12+29)

According to the data obtained, several sites could be suitable for the installation of a WtE plant. However, the weakness of the site model was the lack of available data of the heat and power consumption of the industries that could be useful to determine real utilization factors resulting to much more accurate outcomes of either size, R1 factor as well as gate fee. The same route has been followed in the rest of the cities. In case of Central Greece, due to the fact that the two cities present almost the same characteristics, the examination of a general WtE plant implementation was evaluated. From the results obtained, the proposed algorithm can be applied in each of the selected sites or wherever is possible, also determining the appropriate size of the plant according to the potential of the site to reach maximization of R1 and minimization of gate fee.

Various utilization factors have been taken into consideration and used as the basic parameter for Ep value. From the results obtained, the utilization of energy output is strictly linked, to a great extent, with the formulation of the energy efficiency R1. The higher the utilization factor, the higher R1 values is achieved. However, what should be also highlighted in the forming of the R1 factor is the energy that is inserted into the plant in the form of fuel (Ef). If the amount of solid wastes as feedstock is not stable through the year and the operator of the plant must keep the same power or heat output, due to signed contracts, then large amounts of fuel should be inserted in order to deliver the requested energy. Thus, the specific plant will reach lower values of R1 factor, even less than the minimum authorization value, and therefore will be operating as an only disposal plant D10

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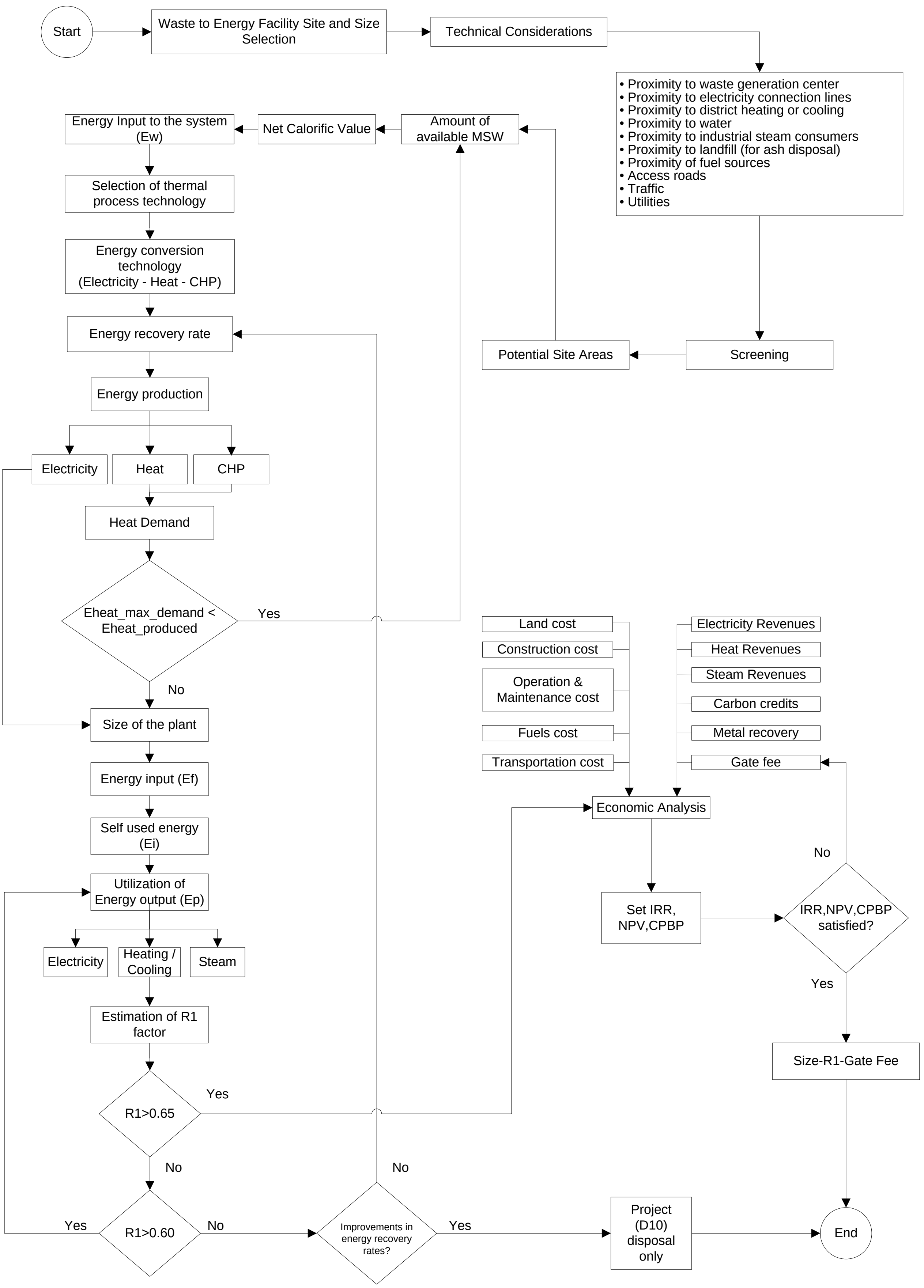


Figure 2. Site and Size selection Algorithm [17]

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When the authorization value of the energy efficiency factor is achieved, then the plant can be characterized as an energy recovery facility. Thus, the estimation of the proper gate fee in order to cope the increased investment cost is achieved through the economic analysis of the project. On one hand the construction, operation and maintenance, as well as the transportation and fuel costs constitute the expenses of the project. On the other hand, the selling power, heat or steam, carbon credits as well as selling from metal recovery constitutes the variable revenues that should be as high as possible. However, the stable revenue of the project, which should be accurate as possible, is the gate fee. From the results obtained, two points should be highlighted.

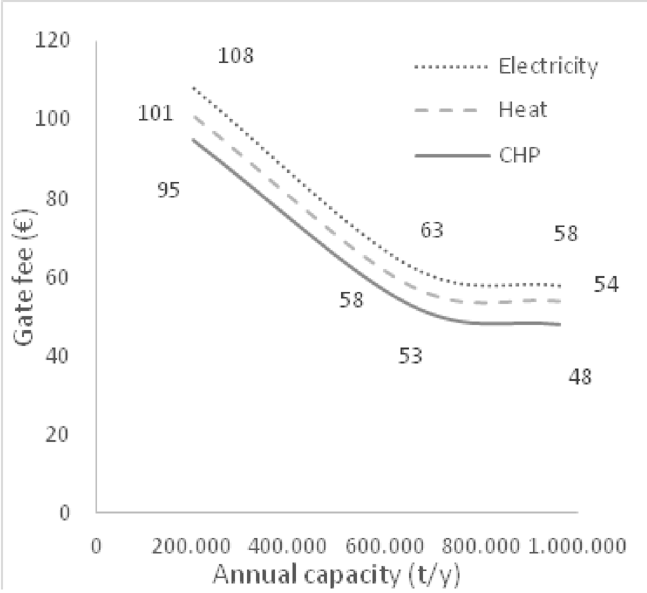


Figure 3. Gate fee based on plant's size.

The first one is the size of the plant. The higher the installed capacity of the plant leads to higher the energy production expected and due to economic of scale lower gate fees is more possible to be achieved. The second one has to do with the utilization factor of the energy output of the plant. The higher the utilization factor, the higher revenues are expected from selling and therefore lead to lower gate fees. What should be emphasized is that the combination of a plant with high installed capacity and high utilization factor constitutes the optimum proposal and when a site could reach both of them, it can be classified as the best one.

4. CONCLUSIONS

This study has developed a fast decision making tool in the form of an algorithm, in order to assess potential sites for their suitability for a WtE implementation taking into consideration various parameters. The model has simulated the change of sites according to the technical considerations provided and determined the total size of the plant. Accordingly, based on various utilization factors of the output energy either when delivered to third parties or for internal use as well as the amount of energy input in the form of fuel, it has simulated the estimation of the energy efficiency factor that could be achieved in each of the investigated sites. Moreover, the algorithm by taking into consideration both expenses and revenues based on the estimated size of the plant, calculated the corresponding gate fee.

From the results obtained, the development of a concrete methodological approach can be feasible in order to assess either a WtE plant that is already in operation or to investigate if a proposed area can be of suitable location for the implementation of such a plant.

Results from the energy efficiency model reveal that the utilization factor of the energy produced plays a major role. Thus, only when high utilization factors are achieved each of the plant can reach maximum energy efficiency factors. Where the energy recovery rates are increased, the energy efficiency factor is increased too or can be increased with lower utilization factors. Waste to energy plants that only produce electricity have the lowest R1 factor in all three case studies. In case of the sites that the plant installed only produces heat, higher energy efficiency factors have appeared compared to an electricity production plant, due to increased energy recovery rates that this technology may provide. The installation of a CHP scheme leads to the highest values of R1 due to the fact of decreased energy imports for the needs of the internal processes as well as due to the potential for the utilization of both forms of energy.

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Finally, from the results obtained the gate fee can be affected by several parameters. From a technical point of view, the higher the energy production has a positive influence. However, it should always be accompanied with high utilization factors. It does not make sense to produce large amount of energy without having the ability to sell it. From an economical point of view, the higher the selling prices the lower gate fee is proposed. Furthermore, the output of the plant may formulate the final gate fee. Thus, it is obvious from the results that the lower gate fee is achieved when a CHP scheme is installed. By the implementation of a CHP scheme in a plant with high installed capacity, as in the case of Athens, the gate fee is the minimum possible (48€) and as the installed capacity of the plant is decreased the gate fee is increased (Figure 3). Concluding, in order for the gate fee to be reduced to the minimum possible, high utilization factors of the plant's output is necessary to be achieved combined with increased installed capacity of the plants.

References

[1] Psomopoulos, C., Themelis, N.J. (2014). A guidebook for sustainable waste management in Latin America. 4th IRRC Conference in Waste to Energy, September 2014, Vienna

[2] Themelis, N.J., Ulloa, P.A. (2007). Methane generation in landfills. *Renewable Energy*, 32(7), pp. 1243-1257.

[3] [DEFRA] Department of Energy and Climate Change, Department for Environment Food & Rural Affairs, United Kingdom (2014). Energy from waste. A guide to the debate.

[4] Agll, A.A.A., Hamad, Y.M., Hamad, T.A., Sheffield, J.W. (2014). Study of energy recovery and power generation from alternative energy source. *Case Studies in Thermal Engineering*, **4**, pp. 92-98.

[5] Themelis, N.J., Barrigga, M.E.D., Estevez, P., Velasco, M.G. (2013). Guidebook for the application of waste to energy technologies in Latin America and the Caribbean. New York: Columbia University, Earth Engineering Centre.

[6] Kiser, J.V.L. (2003). Recycling and Waste-to-Energy: The Ongoing Compatibility Success Story. *MSW management journal*.

[7] Chen, C.C. (2013). Energy recovery or material recovery for MSW treatments?. Resources, Conservation and Recycling, **74**, pp. 37-44.

[8] Hogg, D. (2011). Costs for Municipal Waste Management in the EU: Final Report to Directorate General Environment, European Commission.

[9] [CEWEP] Confederation of European Waste to Energy Plants (2012). Energy report III 2007 – 2010.

[10] Chefdebien, H., Perron-Pique, G. (2014). R1 climate correction factor for waste to energy plants finally agreed. https://waste-management-world.com/a/r1-climate-correction-factor-for-waste-to-energy-plants-finally-agreed.

[11] Perkoulidis, G., Kasampalis, T., Moussiopoulos, N. (2015). Development of Waste-to-Energy plants, database for evaluation the efficiency of energy recovery from waste in Europe. Waste and Biomass Valorization, **6(3),**

[12] [EUROSTAT] (2014). European Statistics.Waste generated. Municipal waste generation and treatment, by type of treatment method.

[13] Stehlik, P. (2009). Contribution to advances in waste-to-energy technologies. *Journal of cleaner production*, **17**, pp. 919-931.

[14] [ELSTAT] (2012) Hellenic Statistical Authority. Census of 2011

[15] Psomopoulos, C., Stavroulakis, S., Stavropoulos, V., Themelis, N. (2013). Greenhouse gases emission reduction potential in Greece by implementing WtE facilities in strategically selected urban areas. Third International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2011) & SECOTOX Conference, 19- 24 June 2011 – Skiathos island, Greece

[16] [ER] EURAC RESEARCH (2012). Analysis of the thermal heating and cooling market in Europe.

[17] Kyriakis E., (2016). *Site and size selection methodology of WtE facilities targeting R1 maximization and gate fee minimization. Case studies: Athens, Thessaloniki and Central Greece.* MSc Thesis. Heriot-Watt University.

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Water saving by applying biosolids to an energy crop under deficit irrigation

D. S. Dimakas, V. Giouvanis, C. D. Papanikolaou, M. A. Sakellariou-Makrantonaki*

Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, GR-38446 Nea Ionia, Magnesia, Greece.
*Corresponding author: Email: msak@agr.uth.gr

Abstract

During the years 2009 and 2010, a study was organized to investigate water saving through the use of Biosolids and deficit irrigation. The experiment was placed at the farm of the University of Thessaly, in Velestino, Central Greece. It was organized four treatments in three replications and the design was Randomized Complete Block. The treatments were: a) Application of biosolids with a provided amount of water equal to the 60% of the daily evapotranspiration needs (ETN), b) Application of inorganic fertilizer with a provided amount of water equal to the 60% of the daily ETN, c) Neither application of fertilizer nor biosolids (untreated control) with a provided amount of water equal to the 60% of the daily ETN, d) Application of inorganic fertilizer with a provided amount of water equal to the 100% of the daily ETN. The combined use of deficit irrigation and biosolids could replace the fertilizer application and save an important amount of irrigation water.

Keywords: biosolids; water saving; deficit irrigation; sweet sorghum; biomass

1. INTRODUCTION

Nowadays, the availability of water for irrigation is a critical factor in agricultural production due to reduced rainfall and their uneven distribution within the growing season. Biosolids and deficit irrigation could help in water saving.

Many cities have a biological waste water treatment plant. One of the final products of the sewage treatment is Biosolids. Plant growth demands nitrogen as well as other inorganic elements such as phosphorus and potassium. Apart from the high levels of organic matter, Biosolids are rich in nitrogen and phosphorus. It is generally recognised that biosolids have beneficial action to the soil as well.

Researches have already shown that if biosolids were used then the soil organic matter and the water holding capacity increase while the soil bulk density decreases [1-3]. Other researchers found that the soil porosity increases and that increase has a negative impact in the soil compaction while it prevents the formation of surface-soil crusts [4]. Furthermore, the soil aeration is improved as well as the root penetration [5]. The same researchers found that Biosolids application also reduce water losses through deep percolation, evaporation, and surface runoff [5].

Biosolids contain high amount of macro- and micronutrients so it can also be an important source of such nutrients for agricultural crops. [6]. Biosolids can change the insoluble form of nitrogen into soluble one so as it can be used by plants more easily. In that way reduces the potential for nonpoint-source pollution, such as that associated with applications of commercial fertilizers [5]. Moreover, plants utilize those nutrients as well as water. Clearly, there are many cases that biosolids could increase yield and improve the quality of the plants' products.

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In the last decades, a word-wide crisis related to energy needs, has dramatically emerged. More energy is needed for industrial purposes as well as to cover the everyday needs of the new facilities and "gadgets" (Smartphones, tablets, GPSs etc.). The main impact is the increased emission of air pollutants in the atmosphere and the hazard they cause to the human health [7]. The Global Warming is still a problem that deals with these pollutants [8]. Therefore, the environment must be protected and the international energy policy must be changed. A reduction of the emitted pollutants and the use of renewable energy could be the first step against environmental pollution. Under that point of view, new development strategies and rules of identifying energy production and consumption must be formed globally. The European Union, which stipulates that by the year 2020 a proportion of 10% of fuel consumed in transport means, in Greece, should be produced from renewable energy sources, is one of those strategies and rules. Generally, 56% of biomass is used to produce energy (renewable source). Specifically, 18% of that percent could be produced by fresh biomass from plants. According to the productivity potential of energy plants, about 5 million hectares with energy plants should be cultivated so as the European Union goals to be fulfilled [8].

Any material derived from living or recently deceased plant and animal organism is characterized as biomass [9]. There are many annual energy crops able to produce stable amounts of biomass. Sorghum is one of them which has a significant yield potential, even in conditions of water stress [10,11]. Sorghum can have two energy destinations: the production of bio-oil charcoal gas, gas, bio-oil, and heat, through thermo-chemical conversion, and the production of ethanol through biological conversion [12]. Sweet sorghum is used for ethanol production because of its high yield of fermentable carbohydrates [13,14].

According to those mentioned above and because sweet sorghum could be a possible alternative crop for biomass and bioethanol production in Greece, in the near future, the present research was organized to study the biomass productivity and water use efficiency of this crop as it might be affected by the application of biosolids and by using deficit irrigation strategies.

2. MATERIALS AND METHODS

The research took place the years 2009 and 2010. The experimental field was located at the farm of the University of Thessaly, in Velestino, Magnesia, Central Greece (latidude 39°23' N, longtitude 22°45' E). The soil is classified as a Typic Xerochrept with a clay loam texture. Each plot covered an area of 32 m^2. The spacing between the plots was 1.5 m. Four treatments in three replications were organized in a randomized complete block design as follows:

a) Biosolids application with supplied amount of water equal to the 60% of the daily evapotranspiration (B60),
b) Inorganic fertilizer application with supplied amount of water equal to the 60% of the daily evapotranspiration (F60),
c) Untreated Control (no application of fertilizer or biosolids) with supplied amount of water equal to the 60% of the daily evapotranspiration (C60),
d) Inorganic fertilizer application with supplied amount of water equal to the 60% of the daily evapotranspiration (F100).

The Municipal Wastewater Treatment Enterprise of Volos supplied the amount of Biosolids which was used. Firstly, the sewage was treated in aerobic tanks under belt filter press. Then the sewage sludge had been dewatered using an innovative infrared radiation processor (IRP) developed by A. Karagiannis (www.eyat.gr). Generally, the Infrared Radiation Process is a method to treat wastewater that achieves direct thermal penetration and has the ability to transport high thermal energy. Moisture and pathogens that are contained in sewage are removed and destroyed by Electromagnetic thermal radiation.

The produced biosolids had less than 10% of moisture and non-traceable pathogens after the treatment with the IRP. Biosolids were distributed by hand one week before sowing at a rate of 5 Mg ha^{-1}. Afterwards it incorporated in the upper 0.2 m of soil depth by rotovation. Biosolids were applied once a year, starting in 2009.

To the treatments where no biosolids applied, an equal dose of inorganic fertilizer was used. That dose of inorganic fertilizer contained the same amount of total nitrogen, phosphorus and potassium as the biosolids. The whole amount of phosphorus and potassium was applied as basal fertilisation one week before sowing, as long as with the 25% of the total nitrogen dose. The fertilizer was spread uniformly in each plot and incorporated in the soil by rotovation in a depth of 0.20m. The remained amount of nitrogen was applied in three equal doses by fertigation, twenty to thirty days after emergence in order to be used efficiently by the plants and minimize losses through the deep percolation.

The sweet sorghum hybrid (Sorghum bicolor (L.) Moench x Sorghum bicolor (L.) Moench 'Sugargraze') was sown at a plant rate of 120.000 plants per hectare early in June for both years. It was used a six-row seeding machine. The spacing between the rows was 0.78 m. After the seed emergence, the same cultivation practices were applied to all treatments. These practices included three weed controls (manual removal).

According to the climatic conditions of the area, during the germination and seedling growth period, sweet sorghum needs about six sprinkler irrigations. The first one was done just after sowing and the last one almost one month later when the plants had developed an adequate root system. The surface drip irrigation program started soon after the last sprinkler irrigation. Drip irrigation laterals were made of polyethylene with a 20 mm nominal diameter. The emmiters were pressure compensated and self-flushed (Netafim™) with an emitter spacing of 0.80 m and a flow rate of 2.3 L h^{-1}. An Evaporation Pan Class A was used to measure the daily Evapotranspiration. The Pan coefficient was found equal to 0.7 for the area. Effective precipitation was calculated as the product of precipitation multiplied by a coefficient according to the rainfall rate (Effective precipitation = Precipitation x coefficient). That coefficient was found equal to 0.8 for the area. The irrigation system was fully automated with electric valves and a programmer. The applied water in each plot was measured with flow meters in order the irrigator to control the system for failures. Furthermore, soil moisture sensors were used in order the soil moisture contain to be measured, especially in the deficit irrigation treatments.

The total amount of irrigation water which supplied through sprinkler and surface drip irrigation methods, for the F100 treatment, was 383 mm during the irrigation period of 2009 and 447 mm for the next irrigation period. The total amount of irrigation water which supplied through the same methods for the B60, F60 and C60 treatments was 264 mm during the first irrigation period (2009) and 306 mm for the second one (2010).

Crop production was measured by means of above-ground biomass. In order the biomass production to be determined all the plants on the middle rows of each plot were harvested, at the milky dough stage. The total production per hectare was determined by weighting the collected plant samples in a precision weight scale. Afterwards the fresh biomass was dried in an oven at 105 ^{o}C until the dry weight to remain steady.

The recorded data during the growing season were analyzed statistically. Analysis of variance (ANOVA) at 5% level of significance was employed to evaluate the statistical effect of deficit irrigation and biosolid application upon sorghum biomass and the water saving. The Minitab Statistical package was used, and Tukey's multiple range tests were applied to evaluate statistical differences between the means of biomass production and water use efficiency [15].

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3. RESULTS AND DISCUSSION

3.1 Climate

Meteorological data were recorded on a daily basis by an automated meteorological station at the farm and compared with the 25-year average values which were based on historical data of the area. The weather station was situated 20 m far from the study's field. The area is characterized by a typical Mediterranean climate with hot and dry summers and cool humid winters. The air temperature and precipitation (10-day average values) prevailing at the experimental field during the growing periods of 2009 and 2010 were compared with an average year and are presented in Figure 1, schematically. The figure below shows that the air temperature during the study period did not fluctuate much from the values of an average year. Generally, in the last 27 years (including 2009 and 2010), the daily average air temperature ranging from about 22 ^oC in mid-June to 25 ^oC in late July, remained almost constant at about 24–25 ^oC during August and dropped in values between 15 and 22 ^oC from late of August to late of September, while it remained below 17 ^oC until the first fortnight of October. The total average rainfall during the whole growing season was 133 mm during the year 2009 and 40mm the next year, while the average precipitation of the last 25 years was 87 mm. Especially, during the years 2009 and 2010, the mean daily air temperature and the mean monthly rain falling did not differ much from the average values of the past 25 years except of the precipitation during the second 10-days of September 2009. Under these circumstances and more generally under the climatic conditions in Central Greece, most summer crops, including sweet sorghum, need irrigation to reach acceptable yields.

3.2 Biomass production

The two-year average of above-ground total biomass production of Sweet sorghum is presented in Figure 2. The maximum dry biomass production was attained by the second half of September (105^{th} day after sowing) for all treatments. Among the treatments where deficit irrigation was applied, the B60 one produced the highest dry biomass, which was 34.9±1.6 Mg ha^{-1}. Second was the F60 treatment which produced a dry biomass of 31.7±1.6 Mg ha^{-1} while in the third place was the C60 treatment with 28.5±0.4 Mg ha^{-1} of biomass production. The full irrigated treatment (F100) produced a dry biomass of 36.1±1.0 Mg ha^{-1}.

The statistical analysis of the data showed that the maximum dry biomass production between the treatments B60, and F100 was not statistically different. However, the other two treatments (C60 and F60) gave statistically different dry biomass production in comparison with the B60 and F100 treatments. Additionally, statistical different was the dry biomass production between F60 and C60 treatments

3.3 Water Use Efficiency

Water use efficiency (WUE) has been the most widely used parameter to describe irrigation effectiveness in terms of crop yield. It was defined by Viets [16] as:

$$WUE = \frac{Y_g}{ET}$$

where WUE is the water use efficiency (kg m^{-3}), Yg is the economic yield (g m^{-2}), and ET is the crop water use (mm). Water use efficiency is usually expressed by the economic yield, but it has been expressed as well in terms of the crop dry matter yield (either total biomass or above-ground dry matter) [17].

The two-year average of water use efficiency of Sweet sorghum is presented in Figure 3. The water use efficiency (kg m^{-3}) for each treatment is expressed as the dry biomass (Mg ha^{-1}) production per total water inputs (mm). It can be observed that the B60 treatment used more efficiently the supplied water. For every cubic meter (m^3) of water the crop, in the B60 treatment, produced

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9.9±1.1 kg of dry biomass, while the F60 treatment produced 9.1±1.0 kg. In the C60 treatment, one m^3 of water was used to produce 8.1±0.5 kg of dry biomass, while in the F100 treatment the same amount of water was used to be produced about 7.5±0.4 kg of dry biomass. On the contrary, for the production of 1 kg of dry biomass, 0.10 m^3 and 0.11 m^3 of water was used by the crop in the B60 and F60 treatments accordingly, while 0.12 m^3 in the C60 treatment and 0.13 m^3 in the F100 treatment.

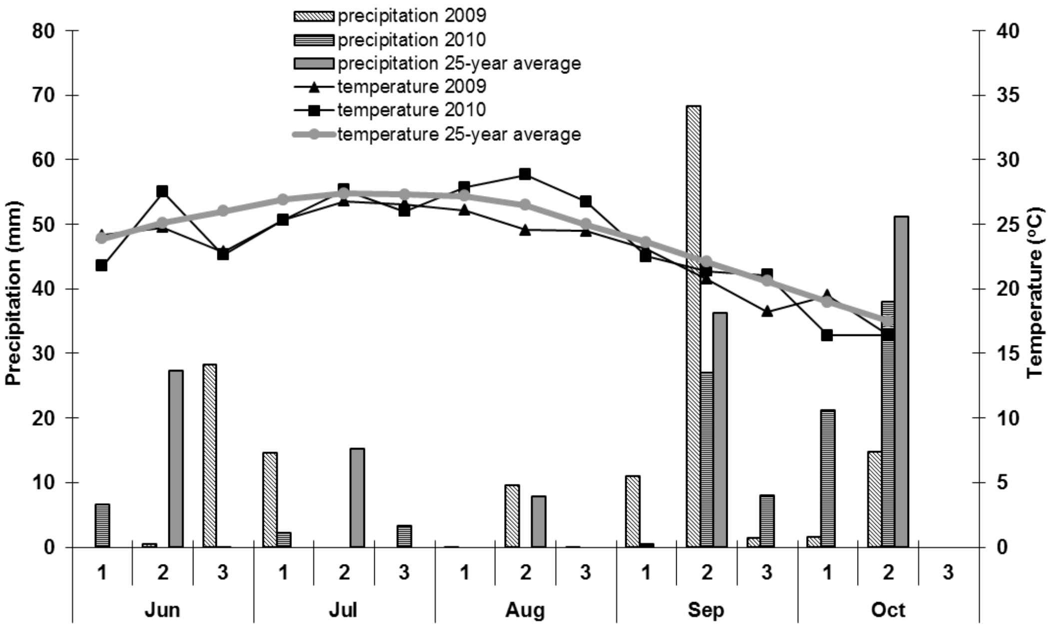


Figure 1. Mean values (10-day periods) of temperature and precipitation for years 2009 and 2010, and 25-year average.

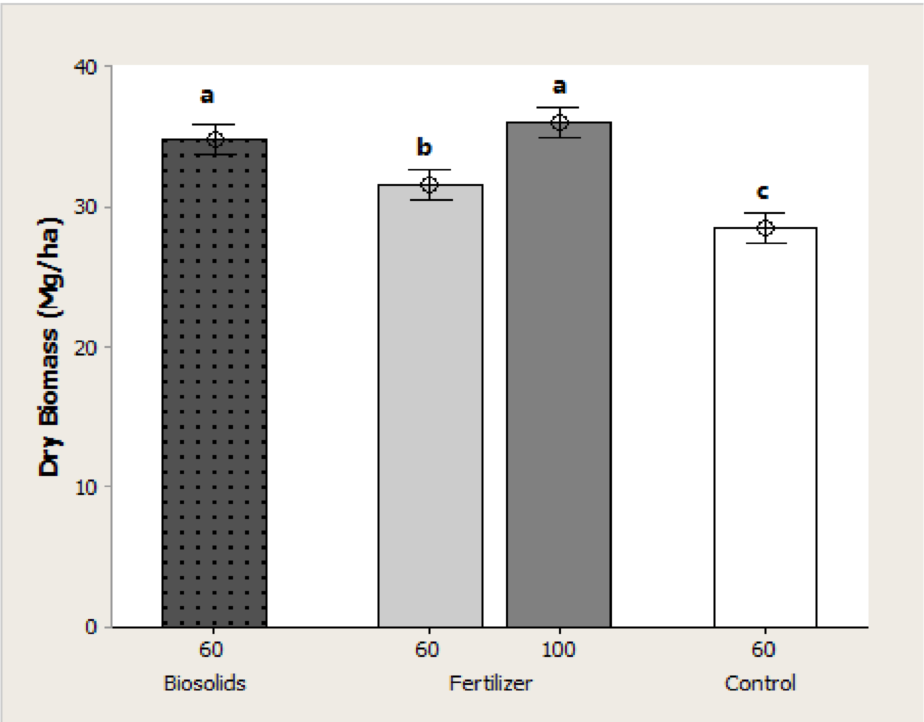


Figure 2. Two year average Dry biomass production of sweet sorghum under different treatments

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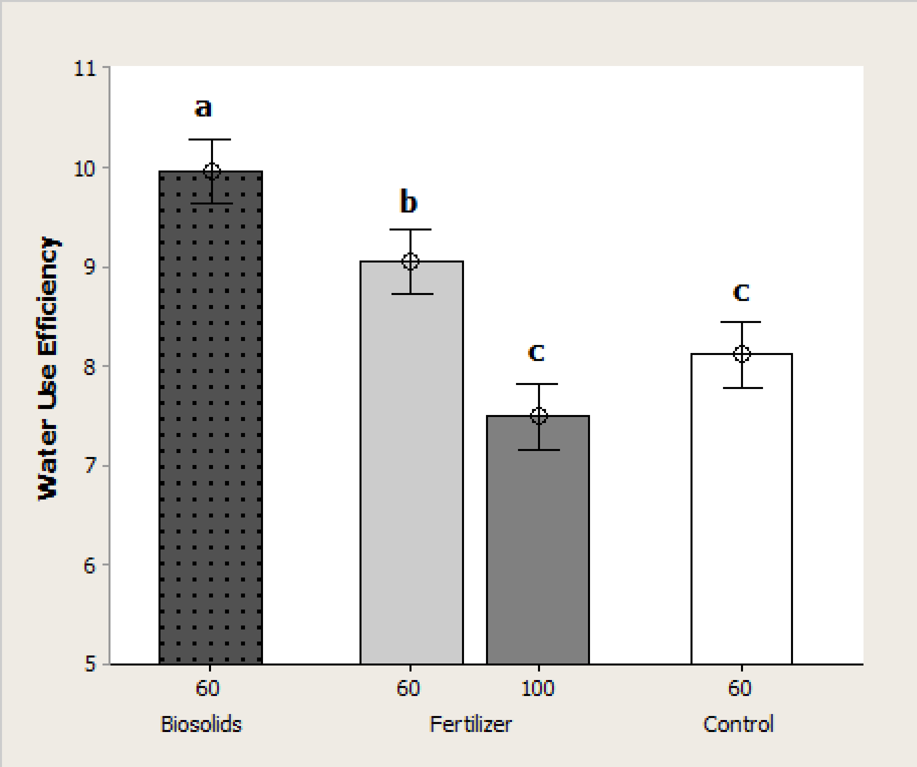


Figure 3. Water Use Efficiency under different treatments.

3. CONCLUSIONS

Based on this study, it can be concluded that under deficit irrigation, sweet sorghum produced higher dry biomass when biosolids was applied in comparison with the inorganic fertilizer application. It seems that biosolids could evenly replace the fertilizer application in terms of biomass production. It also seems that the forms of the nutrients that included in biosolids are more usable from the plant in contrast with the same nutrients from the chemical fertilizers.

The higher Water Use Efficiency was achieved in the treatment that irrigated supplementary and biosolids was used. Specifically, deficit irrigation (60% of evapotranspiration needs) combined with the application of biosolids produced the same dry biomass with the full irrigation treatment (100% of evapotranspiration needs) where inorganic fertilizer was used. This leads to the conclusion that by using deficit irrigation and biosolids 31% of the valuable irrigation water could be saved.

Generally, from the above study is clear that sweet sorghum seems to be a very promising alternative crop for biomass and energy production in Greece in the near future. Additionally, biosolids could be combined with deficit irrigation without any affection in the biomass production in comparison with the full irrigated and inorganic fertigated treatment. This combined irrigation-fertigation program could reduce the application of chemical fertilizers and also save remarkable amount of valuable clean irrigation water. However, an economic analysis could show even an economic benefit to the growers because of the less quantity of irrigation water they need to use and the lower cost to buy biosolids instead of chemical fertilizers. Also, the Municipalities could have an additional economic income as a result of the biosolid sales. Furthermore, it must be noted the environmental benefit from the biosolid use. High amount of unexploited biosolids could be removed from the Municipal repositories where it could be deemed as polluted materials.

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References

[1] Ippolito, A., Barbarick, A., Paschke M. and Brobst, R., 2010. Infrequent composted biosolids applications affect semi-arid grassland soils and vegetation. *Journal of Environmental Management*, 91(5), pp. 1123-1130.

[2] Khaleel, R., Reddy, K. and Overcash, M., 1981. Changes in Soil Physical Properties Due to Organic Waste Applications: A Review. *Journal Environmental Quality*, 10, pp. 133-141.

[3] Powers W.L., Wallingford W.G., Murphy, S.L., 1975. *Research status on effects of land application of animal wastes*. EPA-660/2-75-010, USEPA, Washington, D.C.

[4] Pagliai, M., Antisari, L., 1993. Influence of waste organic matter on soil micro- and macrostructure. *Bioresource Technology*, 43(3), pp. 205-213.

[5] USEPA (1999). *Biosolids Generation, Use, and Disposal in the United States.* EPA530-R-99-009, United States Environmental Protection Agency, Washington, D.C.

[6] Epstein, E., 2003. *Land Application of Sewage Sludge and Biosolids*. CRC Press LLC, Boca Raton, Florida.

[7] Mastrorilli, M., Katergji, N., Rana, G., 1995. Water efficiency and stress on grain sorghum at different reproductive stages. *Agricultural Water Management* 28, pp. 23-34.

[8] Monti, A., Venturi, G., 2003. Comparison of energy performance of fibre sorghum, sweet sorghum and wheat monocultures in northern Italy. *European Journal of Agronomy* 19, pp. 35-43.

[9] http://www.biomassenergycentre.org.uk (accessed November 11, 2008).

[10] Cosentino, L., 1996. Crop physiology of sweet sorghum. *Proceedings of 1st European Seminar on Sorghum for energy and industry*, 1–3 April 1996, Tulose, pp. 30–41.

[11] Foti, S., Cosentino, S., Copani, V., Patane, C., Guarnaccia, P., 1996. Growth and yield of C4 species for biomass production in Mediterranean environment. *Proceedings of 9th European Bioenergy Conference: Biomass for energy and environment*, June 1996, Copenhagen, Denmark, pp. 616–621.

[12] Venturi, P., Venturi, G., 2003. Analysis of energy comparison for crops in European agricultural systems. *Biomass and Bioenergy*, 25, pp. 235-255.

[13] Dolciotti, I., Mambelli, S., Grandi, S., Venturi, G., 1998. Comparison of two Sorghum genotypes for sugar and fiber production. *Industrial Crops and Products*, 7, pp. 265-272.

[14] Whitfield, B., Chinn, M., Veal M., 2012. Processing of materials derived from sweet sorghum for biobased products. *Industrial Crops and Products*, 37(1), pp. 362-375.

[15] Montgomery, C.D., Runger, C.G., 2003. *Applied statistics and probability for engineers, 3rd edition.* Wiley, London, pp 468–499.

[16] Viets, G., 1962. Fertilizers and the Efficient Use of Water. *Advances in Agronomy*, 14, pp. 223-264.

[17] Howell, A., 2001. Enhancing Water Use Efficiency in Irrigated Agriculture. *Agronomy Journal*, 93, pp. 281-289.

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Effect of wheat biochar on silt soil temperature in coal mines located in arid-semiarid areas in China

J. Xiong*, Z. Bian, S. Lei, D. Yang, T. Wang

School of Environmental Science & Spatial Informatics, China University of Mining and Technology, Xuzhou 221008, China.
*Corresponding author: Email: xiongjib108@163.com

Abstract

Most coal mines are located in arid-semiarid areas in China, 90% of which belong to well mining, resulting in serious soil disturbance. Moreover, the difference of air temperature in these arid-semiarid areas is very large between day and night, therefore soil temperature (one of key influencing factors of plant growth) is easily influenced by soil disturbance. At the same time, wheat straw burning has resulted in serious air pollution in China. In this paper we studied the effect of wheat biochar (1%, 2% and 4%) on different depth of soil temperature at different soil humidity (10%, 20% and 30%) and air temperature: 50°C and air humidity: 40%. the results showed that wheat biochar could obviously increase the heat capacity of the soil, and the trend increased with an increase of soil moisture. Wheat biochar could reduce the coefficient of heat conductivity and thermal diffusivity. Soil temperature was mainly controlled by soil depth and soil humidity, and the appropriate wheat biochar concentration could decrease soil temperature especially at high air temperature and high soil humidity, which is useful for plant growth. Wheat biochar may be useful for soil temperature modification in coal mines in arid-semiarid areas in China.

Keywords: wheat biochar; arid and semiarid areas; coal mining; soil temperature; thermal parameters.

1. INTRODUCTION

Soil temperature is an important variable influencing a range of physical, chemical, and biological processes occurring in the soil [1,2]. The soil temperature is significantly influenced by variable soil content, bulk density, organic matter, soil texture and air temperature [3,4]. Forty percent of the global land surface is an arid or semiarid climate. How mining affects soil has been an important research field for decades. Half of the total coal reserve of China IS found in arid-semiarid areas such as Shanxi Province, Inner Mongolia, Gansu Province, Ningxia Province and Shanxi Province [5]. 90% of coal mining belongs to underground mining in these coal mining areas. Coal exploitation have left these regions with a legacy of severe water shortage, destroyed soil, and damaged irrigation infrastructures [6]. More soil was disturbed and exposed to air due to surface cracking and subsidence of the topsoil by underground mining in these coal mining areas [7], and more easily influenced by air temperature. Moreover, as the climates of these regions become warmer, the maximum air temperature can reach 50°C during Summer [8]. Warmer temperatures may accelerate soli organic carbon (SOC) decomposition in these mining areas. Potential decrease in SOC quality in response to warming and consequent shifting species composition may result in a positive feedback of SOC to climate change in the future [9].

At the same time, field burning of wheat straw is a common practice in many countries, which emits trace and particulate matter leading to deleterious impact on earth’s atmosphere. They have

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harmful impact on human health, natural environment and ecological system [10]. Many state and national governments have enforced legal restrictions on field burning as a result, and in China these bans are enforced at a cost of millions of dollars each year [11]. In China wheat straw residues are ordered to be remained in the field after crushing. However, it increases crop diseases which sometime reduces crop yield [12]. In this scenario, biochar, a pyrolysed product of biomass offers an opportunity to transform large scale agricultural waste streams from a financial and environmental liability to valuable assets.

Recently, there has been paid attention in biochar application to soil for several potential benefits: carbon sequestering, bioenergy generation, reduction of hazardous gas from soil, sorption of nutrient ions, improvement in soil structure and retention of soil moisture [13]. However, a few studies on soil temperature [14]. In this research, biochar from wheat straw was studied on silt soil temperature. The objective of this study was to assess the effect of different concentration of wheat biochar on silt soil temperature at different soil depths and soil moisture under high air temperature and low air moisture. It was expected that the research results would be useful for understanding the effect of the wheat biochar on response of slit soil temperature in coal mines to high air temperature under semiarid climate.

2. MARERIALS AND METHODS

2.1 Soil

Soil was collected from DaLiuta coal mining areas in Yulin city, Shanxi Province, China. The soil type belongs to Chestnut soil and texture is silt soil (USDA classification) with 0.11% sand, 96.86% silt and 2.93% clay (Fig. 1). The soil was air dried and was passed through a 2 mm mesh for the soil temperature experiment. It has pH 8.94 (1:5 soil/water suspention; PHS-3B), electrical conductivity (EC) 82 us cm^{-1} (1:5 soil/water suspension; HM AP-2), total organic carbon: 2.7g kg^{-1} (Elementar, Vario TOC Cube, Germany). Soil particle composition was analyzed by laser diffraction using a Rise-2006 particle size analyzer (Runzhi instruments, China).

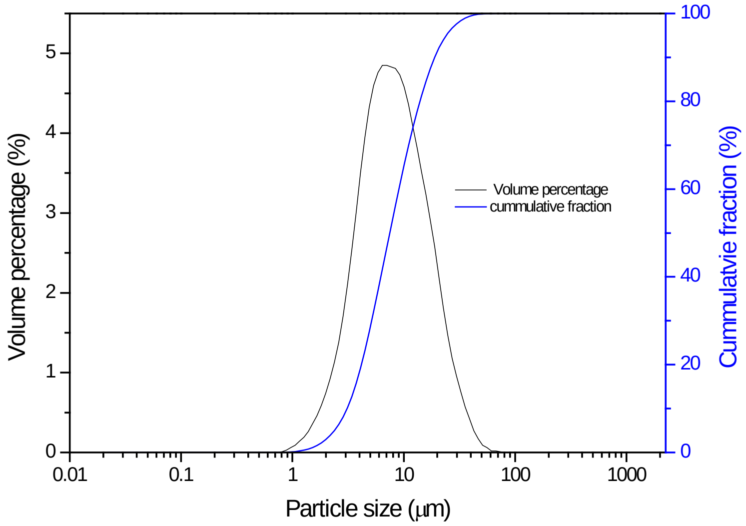


Figure 1. Particle size distribution of experimental soil

2.2 Wheat biochar preparation

Wheat straw was used to produce biochar under anoxic conditions by biochar reactor. Prior to biochar production, the wheat straw was oven-dried for 12 h at 80°C, and then moved to the biochar reactor, which was heated to 320°C, and held constant for 1 h, After heating for 2 h, the reactor was

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switched off. The wheat biochar sample was cooled to room temperature, and sieved through a 2-mm mesh and about 40% of dried wheat weight was converted to biochar.

2.3 The effect of wheat Biochar on silt soil temperature

The experimental silt soil containing 0%, 1%, 2% and 4% wheat biochar was made 10%, 20% and 30% moisture (w/w) by adding deionized water, then the samples were loosely placed in 16 cm diameters PPR pipe enclosed with heat consult materials, which make heat transfer from the pipe top to the pipe bottom, simulating field conditions. The experiments were performed in artificial climate chest. The air temperature and humidity of the artificial climate chest were controlled at 50°C and 40%, respectively. Initial silt soil temperature is about 30°C. The soil temperature was examined at 5cm, 10cm and 15cm depth every half a hour by soil thermalmeters.

2.4 Data analysis

The differences between wheat biochar addition and no wheat biochar addition were also statistically evaluated at 5% probability level by two-way ANOVA in SPSS 18. The representation and graphical fits of experimental data were obtained by using Origin 8.0.

3. RESULTS AND DISCUSSION

3.1 The effect of wheat biochar concentrations on sandy loam soil heat parameters

The thermal conductivity, thermal diffusivity, and volumetric heat capacity are basic three soil thermal parameters which are related with soil temperature. The thermal diffusivity can reflect soil temperature and heat flux [15]. It can be seen from Table 1 that thermal conductivity decreased with an increase of wheat biochar concentrations under the same soil moisture. But it did not reach significant levels ($P < 0.05$). While thermal conductivity increased significantly with an increase of soil moisture under same wheat biochar concentration addition ($P < 0.05$), which favors heat flux and an increase rate of silt soil temperature under high air temperature. Mass specific heat capacity increased significantly with wheat biochar concentrations and soil moisture increase ($P < 0.05$), which slows silt soil temperature rise rate under same heat input.

Table 1. Thermal parameters of different moisture soil with different concentrations of wheat biochar

Treatment	Water content (%)	Density (kg/m^3)	Thermal conductivity (W/m °C)	Mass specific heat capacity (J/kg °C)	Thermal diffusivity (10^{-3}cm^2/s)
0% wheat biochar	10.0	1790	1.17	1082.1	6.04
1% wheat biochar	10.0	1380	0.87	1164.4	5.41
2% wheat biochar	10.0	1300	0.68	1173	4.46
4% wheat biochar	10.0	1370	0.47	1157	2.97
0% wheat biochar	20.0	2270	2.01	1233.4	7.18
1% wheat biochar	20.0	2220	2.08	1314.7	7.13
2% wheat biochar	20.0	1930	1.67	1324.9	6.53
4% wheat biochar	20.0	1710	0.88	1328.7	3.87
Wheat biochar	1.4	180	0.06	1169.5	2.85
Wheat	1.4	300	0.21	887	7.89

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Thermal diffusivity obviously decreased with the increase of wheat biochar concentrations or soil moisture ($P < 0.05$). The effect of 4% wheat biochar on silt soil thermal diffusivity is significant compared with 0%, 1% and 2% wheat biochar ($P < 0.05$). It can be seen from above analysis that the soil thermal parameters are also influenced by soil moisture [16], but the influence of soil moisture on the soil thermal parameters is complex [17].

3.2 The effect of wheat biochar concentration on soil temperature under different soil moisture

As shown in Figure 2A, under the silt soil moisture is 10%, the silt soil temperature at 5 cm depth increased quickly in first 0.5 h but increase rate gradually decreased with time and a decrease of difference between soil temperature and air temperature. In the end of the experiment (4 h), the temperature of 5 cm silt soil depth with 0%, 1%, 2% and 4% wheat biochar are 37.9°C, 38.4°C, 38.0°C and 38.2°C, respectively.

Soil temperature increase rate also decrease with an increase of soil depth whether wheat biochar addition or not (Figure 2) except for the soil temperature at 10 cm depth which showed temperature accumulation as compared with other depths. Although wheat biochar increased silt soil temperature in comparison to no wheat biochar addition, the differences are very small at the end of the experiment (4 h). In all the treatments, 2% wheat biochar concentration minimized increase rate of silt soil temperature as a whole compared with other wheat biochar concentrations. This may be attributed to higher concentration of black wheat biochar absorbing more energy.

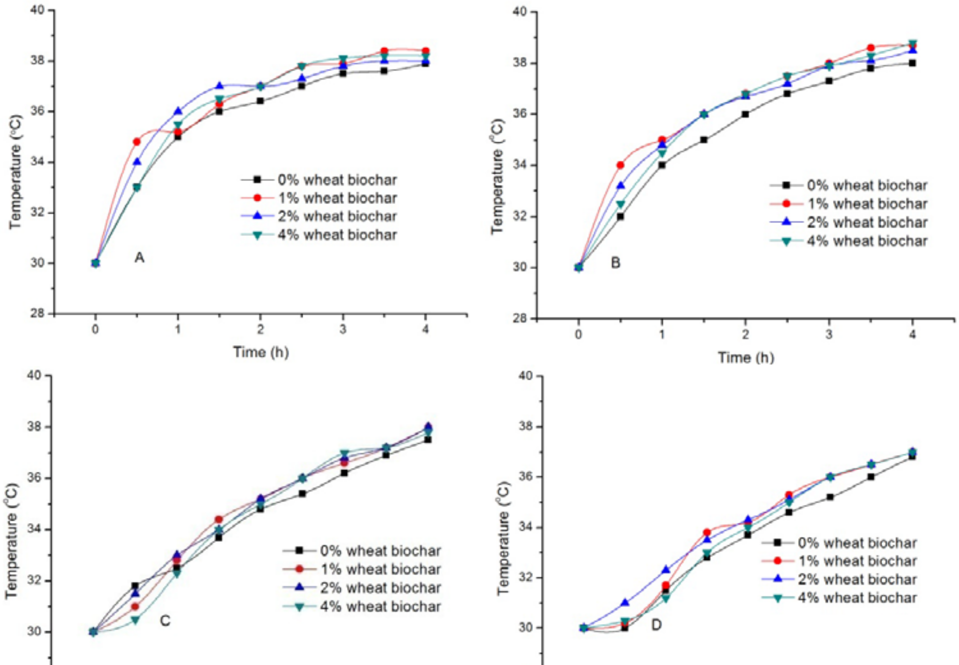


Figure 2. Effect of wheat biochar on A: 5cm, B: 10cm, C: 15cm, and D: 20cm soil temperature at initial soil moisture: 10%, air temperature: 50°C and air humidity: 40%.

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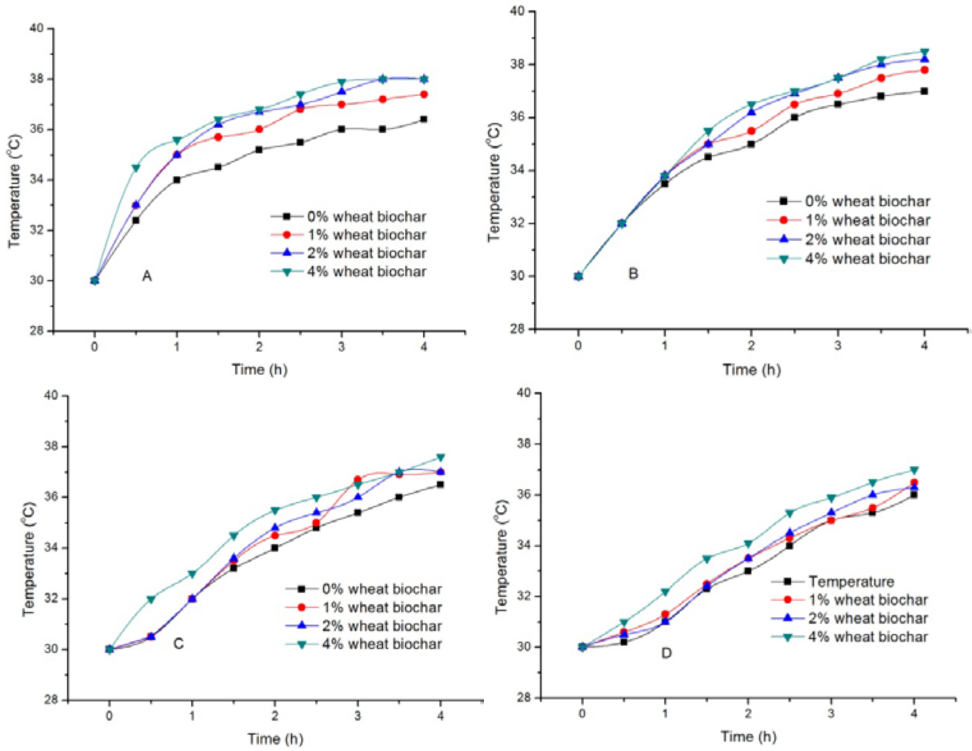


Figure 3. Effect of wheat biochar on A: 5cm, B: 10cm, C: 15cm, and D: 20cm soil temperature at initial soil moisture : 20%, air temperature: 50°C and air humidity: 40%.

The results in Figure 3 showed that the increase rate of the silt soil at the same soil depth generally decreased compared with the results in Figure 2, which proved that an increase of silt soil moisture favored a decrease of silt soil temperature increase rate. It can be found in Figure 3 that although increase rate pattern of the silt soil with 20% soil moisture at the same soil depth was similar in comparison with 10% soil moisture (Figure 2), the increase rate differences of the silt soil with 20% soil moisture between wheat biochar addition and no wheat biochar addition gradually widened. For example, the temperature of the 5 cm silt soil depth with 0%, 1%, 2% and 4% are 36.4°C, 37.4°C, 38.0°C and 38.0°C, respectively (Figure 3A). As seen from Figure 3. It also can be seen from Figure 3 that 1% concentration wheat biochar showed good effect at almost different soil depth while 2% also showed almost same effect at 15 cm and 20 cm soil depths compared with 1% wheat biochar.

Figure 4 presents the effect of different wheat biochar on silt soil under high soil moisture (30%) and low air humidity (40%). On the whole, the increase rate of the temperature of the silt soil with 30% soil moisture further decreased compared with 10% or 20% soil moisture (Figure 2 and Figure 3). For example, the temperature of the 5 cm silt soil depth with 0%, 1%, 2% and 4% are 37.0°C, 35.0°C, 35.2°C and 37.6°C, respectively (Figure 4A), while the temperature of the 20 cm silt soil depth with 0%, 1%, 2% and 4% are 35.7°C, 34.5°C, 34.8°C and 37.3°C, respectively (Figure 4D). As can be found in Figure 3, the rising rate of temperature of the silt soil decreased with an increase of biochar (1% and 2% wheat biochar) in comparison to no biochar addition while 4% biochar addition increased the rising rate of temperature of the silt soil compared with no biochar addition.

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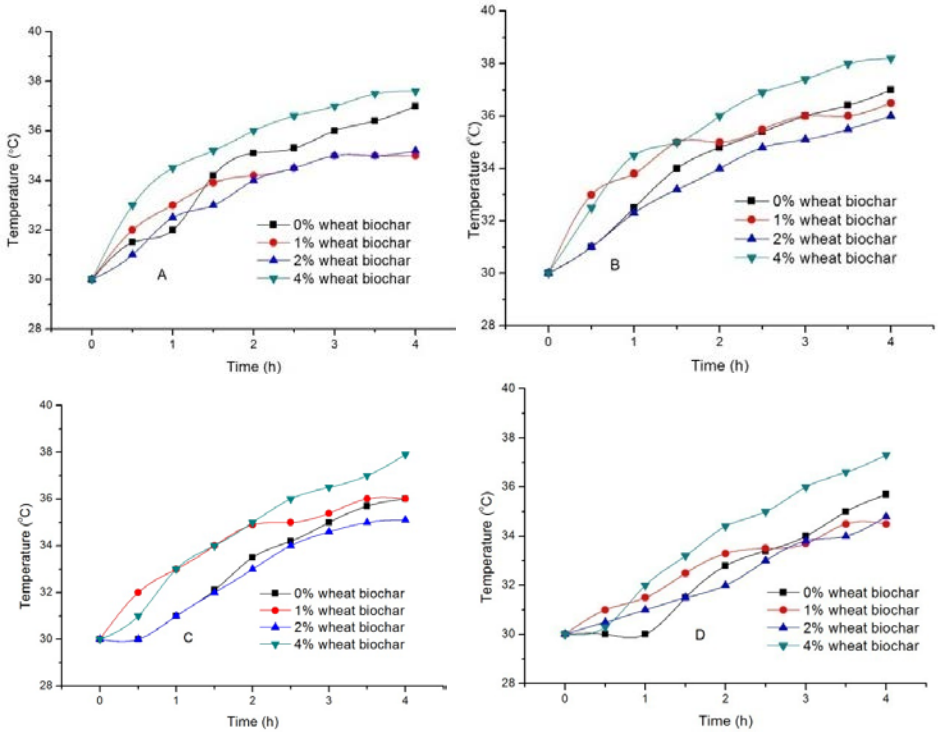


Figure 4. Effect of wheat biochar on A: 5cm, B: 10cm, C: 15cm, and D: 20cm soil temperature at initial soil moisture: 30%, air temperature: 50°C and air humidity: 40%.

4. CONCLUSIONS

The increasing of wheat biochar concentrations in the silt soil are benefit for decreasing thermal conductivity and increasing thermal diffusivity under 10% and 20% moisture. But the effect of wheat biochar on soil temperature depends mainly on soil moisture and soil depths under the condition of high air temperature and low air moisture. 1% and 2% wheat biochar showed good effect under different soil depth and soil moisture, especially under high soil moisture (30%).

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References

[1] Hillel, D., 1998. Introduction to Environmental Soil Physics, Elsevier Academic Press, London.

[2] Khoshkhoo, Y., Jansson, P.E., Irannejad, P., Khalili, A., Rahimi, H., 2015. Calibration of an energy balance model to simulate wintertime soil temperature, soil frost depth, and snow depth for 14 year period in a highland area of Iran. *Cold Regions Science and Technology*, **119**, 47-60.

[3] Abu-Hamdeh, N.H., Reeder, R.C., 2000. Soil thermal conductivity: effects of density, moisture, salt concentration, and organic matter, *Soil Science society of America Journal*, **64**, 1285-1290.

[4] Mosier, A.R., 1998. Soil processes and global change. *Biology and Fertility of Soils*, **27**, 221-229.

[5] Lei, S., Bian, Z., Daniels, J.L., He, X., 2010. Spatio-temporal variation of vegetation in arid and vulnerable coal mining region. *Mining Science and Technology*, **20**, 0485-0490.

[6] Qian, M.G., 2003. Technological system and green mining concept. *Coal Science & Technology Magzine*, **4**, 1-3.

[7] Tripathi, N., Singh, R.S., Singh, J.S., 2009. Impact of post-mining subsidence on nitrogen transformation in southern tropical dry deciduous forest, China. *Environmental Research*, **109**, 258-266.

[8] Wang, X., Guo, W., Zhong, Z., Cui, X., 2009. Long term trends of soil moisture and temperature change in East China in relationship with climate background. *Advance Earth Science*, **24**,181-191 (in Chinese).

[9] Xu, X., Luo, Y., Zhou, J., 2012. Carbon quality and the temperature sensitivity of soil organic carbon decomposition in tallgrass prairie. *Soil Biology & Biochemistry*, **50**, 142-148.

[10] Cheng, Z.L., Lam, K.S., Chan, L.Y., Wang, T., Cheng, K.K., 2000. Chemical characteristics of aerosols at coastal station in Hong Kong. I. Seasonal variation of major ions, halogens and mineral dusts between 1995 and 1996. *Atmospheric Environment*, **34**, 2771-2783.

ISBN: 978-960-6865-94-7

[11] Clare, A., Barnes, A., McDonagh, J., Shackley, S., 2014. From rhetoricto reality: farmer perspectives on the economic potential of biochar in China. *International Journal of Agricultural Sustainability*, **12**, 440-458.

[12] Cook, R.J., Haglund, W.A., 1991. Wheat yield depression associated with conservation tillage caused by root pathogens in the soil not phytotoxins from the straw. *Soil Biology and Biochemistry*, **23**, 1125-1132.

[13] Lone, A.H., Najar, G.R. Ganie, M.A., Sofi, J.A., Ali, T., 2015. Biochar for sustainable soil health: a review of prospects and concerns. *Pedosphere*, **25**, 639-653.

[14] Zhang, Q., Wang, Y., Wu, Y., Wang X., Du, Z., Liu, X., Song, J., 2013. Effects of biochar amendment on soil thermal conductivity, reflectance, and temperature. *Soil Science Society of America Journal*, **77**, 1478-1487.

[15] Zhang, H.H. Liu, S.H. Wei, Z.G. Lu, S.H. Hou, X.H. Wen, J. Cao, X. Q., 2011. Comparative study of computing methods of soil temperature on different underlying surfaces. *Acta Scientiarum Naturalium Universittatis Pekinensis*, **47**, 1025-1033.

[16] Tong, B., Gao, Z., Horton, R., Li, Y., Wang, L. 2016. An empirical model for estimating soil thermal conductivity from soil water content and porosity. Journal of Hydrometeorology, **17**, 601-613.

[17] Lu, S., Ren, T. S., Gong, Y.S., Horton, R., 2007. An improved model for predicting soil thermal conductivity from water content. *soil Science society of America Journal,* **71,** 8-14.

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An island landfill mining and municipal solid waste treatment approach

I. Frantzis[*], D. Skoura

I. Frantzis & Associates Ltd, 30, An. Zinni str.,Koukaki, 11741, Athens, Greece.
*Corresponding author: Email: frantzis@i-frantzis.com

Abstract

An Integrated Solid Waste Management system involves measures and actions focusing on all aspects of Waste Treatment. This principle is especially strengthened within the European Legislation that sets quantitative & timeframe standards for Recycling and Biodegradable fraction diversion rates. Especially the Greek MSW National Plan imposes a 65% Recycling & a 40% Organics source separation rate. At the same time landfill diversion rate of biodegradables is set to 65%, while the final residues to be landfilled should be less than 30% of MSW produced.

Greek islands have some special characteristics, thus different solid waste management solutions should be implemented. More specifically, Greek islands are characterized by:

- Limited available land and resources.
- Significant population growth during the tourist period.
- Great dependence of the local economy on tourism.
- Difficulty in the implementation of a common SWM policy with mainland.

The above characteristics in combination with the need for adaptation to the current MSW legislation dictate the adoption of a specific SWM model applicable to small-medium size communities such as islands. Thus "MSW Treatment (MSW/T) plus Landfill Mining (LFM)" is considered as an ideal approach. The system has been analysed in depth by Frantzis & Associates Ltd and is nearly ready to proceed with the implementation stage.

The proposed paper will explain the fundamentals of the technologies incorporated and their applicability to the island MSW treatment & disposal approach. The application of this scale and nature is an important element in this equation. Emphasis will be given to the «economies of scale» when the technologies of MSW/T and LFMR are merged, with operational results being presented and explained.

Keywords: solid waste management (SWM); landfill mining (LFM); municipal solid waste treatment (MSW/T)

1. INTRODUCTION

Landfill mining & Reclamation (LFMR) is a process whereby solid wastes which have previously been landfilled are excavated and processed typically from an active or closed landfill. LFMR aims to the accomplishment of one or more of the following purposes: “conservation of landfill space, reduction in landfill area, expansion of landfill lifetime, elimination of a potential source of contamination, mitigation of an existing contaminated source, energy recovery from excavated waste, recycling of recovered materials, reduction in waste management system costs and site re-development” [1].

Processing typically involves a series of mechanical processing operations designed to recover one or all of the following: recyclable materials, a combustible fraction, soil and landfill space. In addition, LFMR can be used as a measure to remediate poorly designed or improperly operated

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landfills and to upgrade landfills that do not meet environmental and public health specifications [12].

Waste disposal in landfills and dumpsites represent the most popular way of waste treatment in many countries of the world [2, 11]. Concerning Europe, it is estimated that the total number of landfills and old dumpsites (operational and closed) is around 150-500.000 [6, 7]. The Council Directive 1999/31/EC on the landfill of waste was voted by the Council of the European Union in 26 of April 1999. The major aim of this Directive is to "*provide for measures, procedures and guidance to prevent or reduce as far as possible negative effects on the environment, in particular the pollution of surface water, groundwater, soil and air, and on the global environment, including the greenhouse effect, as well as any resulting risk to human health, from landfilling of waste, during the whole life -cycle of the landfill*".

Municipal Solid Waste Treatment can be considered as an **Integrated MSW Processing** Line having the capability of co-processing Source Separated Organics (SSO). The advantages of this application are a) low investment cost, b) low operating expenses, easiness of sitting, as mobile equipment and d) minimum environmental impacts.

The processing line includes a) mobile shredding unit with Fe separator, for shredding all incoming MSW and removing ferrous metals, b) mobile separation unit for the separation of shredded MSW into organic & non-organic fractions, c) mobile unit for composting in closed system – in tunnel composting – of the MSW organic fraction as well as the SSO in separate lines, d) mobile MRF for recovery of recyclables and e) mobile baler for baling the process residuals.

2. MATERIALS AND METHODS

The overall objective of this paper is to present a landfill mining project in Greece, in conjunction with fresh MSW treatment in a typical small to medium scale Greek island. More specifically, the idea is to consider these two activities into a single package (the Project). The Project provides that the Landfill Site will not undergo the typical remediation process, instead Landfill Mining and Reclamation (LFMR) will start, while at the same time fresh MSW will be Treated (MSW/T) on the same site. As a result reduced remediation costs, revenues from selling recyclables, as well as an indirect profit from reusing the same site for landfilling – thus avoiding expenses - are expected.

The Landfill Mining and MSW Treatment Project ($MSW/T \sqrt{LFMR}$) Project combines a series of methods for the accomplishment of site remediation and fresh MSW treatment. First an extended literature review was conducted in order to gain a thorough understanding of the LFMR method before proceeding with the analysis of the proposed LFMR project.

The organization of the Project requires the collection and inventory of information material concerning the region, the characteristics of the dumpsite and in general the current situation of the dumpsite. Thus the methods used for the collection and inventory of the above information are briefly presented below:

- Previous Studies conducted for the specific Landfill Site (LS)
- Visits of the project team work to the Project's area
- Face to face interviews with the competent bodies (Municipality).

The *typical* Site covers an area of 15.000m^2 and the amount of waste already disposed of is approximately 50.000 tons or 65.000m^3, to which a quantity of approximately 7.500m^3 of cover material must be added. Disposal of waste is still being carried out in the same area, therefore it is of paramount importance to proceed with the remediation of it.

However, due to the organic materials degradation and settlement the above figure does not represent the current volume which is estimated as to 55-60.000m^3.The proportion of MSW in the LS is estimated to 95% of the total volume, the rest being inert material.

At the same time, the amount of fresh incoming MSW is approximately 10.000ton/y, out of which approximately 1.600ton/y will be Source Separated Organics (SSO) [4, 5, 8, 9, 10].

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3. RESULTS AND DISCUSSION

3.1 Description of the Project

The proposed Project combines the remediation of this *typical* LS and Treatment of fresh MSW at the same time, thus it requires the implementation of LFMR principle as well as MSW Management for the coming years.

The Concept of the Project may be described in the following equation: $MSW/T\ \sqrt{LFMR}$. The proposed holistic Waste Management incorporates two (2) mobile Units so that Treatment of fresh MSW will take place in parallel to cleaning the area through Removal of Disposed Waste and Recovery of useful materials.

3.1.1 Description of the Mobile Materials' Recovery Unit

As mentioned earlier in the paper the current volume of the disposed waste is 62.500-65.000m^3 or 50.000 tons that should be excavated during a period of five (5) years, thus the Unit will have a capacity of 10.000tons/y or 40tons/d (operation for 260 d/yr, five days per week, 8hrs/d).

The LFMR Unit will include a list of equipment such as excavators, trommel, conveyors, magnet separator, system of controlling dust releases.

3.1.2 Operation of the LFMR Unit

The Unit will conduct the following waste treatment process:

- Mechanical excavation of dumped waste having a capacity of 10.000 tons per annum.
- Pre-screening for the removal of bulky items.
- Separation through the trommel and removal of the fine fraction, which will be used for quarry restoration or as soil cover in the surrounding area. The coarse fraction remains in the system and is loaded on the conveyor.
- Drum Magnet for the separation of ferrous metals. The non-magnetic fraction remains in the system.
- Manual sorting of recyclables (plastic, aluminum, glass) in the conveyor. It is anticipated that the system will be manned with six to seven hand pickers.

The recovered materials are collected in 100-150lt or bigger, 660-1.100lt ones, so that they are temporarily stored until being transported to the local Recycling Centre. It is worth mentioning that all waste streams (incoming and outgoing from the Unit) will be recorded, monitored and measured. Finally, the residues from LFMR Unit will follow the same route as the ones from Municipal Solid Waste Treatment Unit (baled and stored).

The flow diagram of the process is presented in the following figure (Figure 1).

3.2 Description of fresh Municipal Solid Waste Treatment (MSWT) Unit

The capacity of the second Mobile Waste Treatment Unit will be 10.000tn/year or 45tn/day, out of which 1.600tn/y will consist of Source Separated Organic (SSO) waste. Both, the treatment of mixed incoming MSW and SSO will take place through the mobile waste treatment Unit.

The mixed MSW/T partly consists of mechanical treatment and partly of Biological one. More specifically, the equipment needed is the following:

- Weighbridge
- Bag opener & Shredder
- Trommel
- Mobile Sorting Unit
- Composting Unit
- Mobile Baling System
- Office
- Compact Unit for (any) leachate treatment.

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3.2.1. General Process Description

The trucks, after the weighbridge, will gradually deposit the waste in the reception area. The bulky objects will be removed and waste will be channelled to the bag opener/shredder. In the shredder all the materials are homogenized, after being shredded in up to 300mm pieces.

The shredded waste pass through metal or magnetic separator for ferrous materials removal. The waste is then forwarded to a specific mobile separator/trommel, suitable for the separation of organic materials from the rest of waste. The two streams are:

a. Recyclable materials (fine fraction) that undergoes further treatment (separation / recovery / screening) and
b. Organics that is forwarded for composting.

3.2.2. Stream of Recyclables

The >75mm fraction is forwarded to the container type Sorting Platform, where materials such as plastic, glass, non-ferrous metals, wood, paper, fabrics are separated. The recovered materials are collected in plastic bins, temporarily stored in suitable waste boxes or baled until further forwarded to the Recycling Centre.

The residues remaining after the manual sorting line will be forwarded to the LS for disposal.

3.2.3. Organic Stream

The organic fraction, received from the trommel, is forwarded to the mixer where the desired green-to organic ratio is achieved. The shredded green waste will be the "building material" of the process, improving the quality of final product and facilitating the biodegradation. Then the homogenized material will be placed in a closed bag for aerobic treatment (composting). The bags are placed close to each other not only to use the area optimally but also to use the heat from neighbouring bags to avoid cold zones in the winter time. The main composting process in the bag takes between 10-12 weeks.

Post-composting – maturation - phase then follows. Temperature control and aeration ensures a safe and stable compost product.

The same procedure is followed for the SSO stream, as well.

3.2.4. Mobile Baling System

The mobile Baling System is mainly used during the last stage, where the process residuals are compressed and baled for temporary storage.

3.2.5. Mass Balance

According to the existing Law, the National Waste Policy is oriented towards the following goals for the year 2020:

- Per capita waste generated should be drastically reduced.
- Preparation for reuse and recycling with source separation of recyclables & organic waste should reach 50% of MSW. More specifically, source separation of packaging materials should reach 65% while the target for biodegradables should be 40%.
- Sanitary landfill should be the last option and should be restricted to less than 30% of MSW produced. [3]

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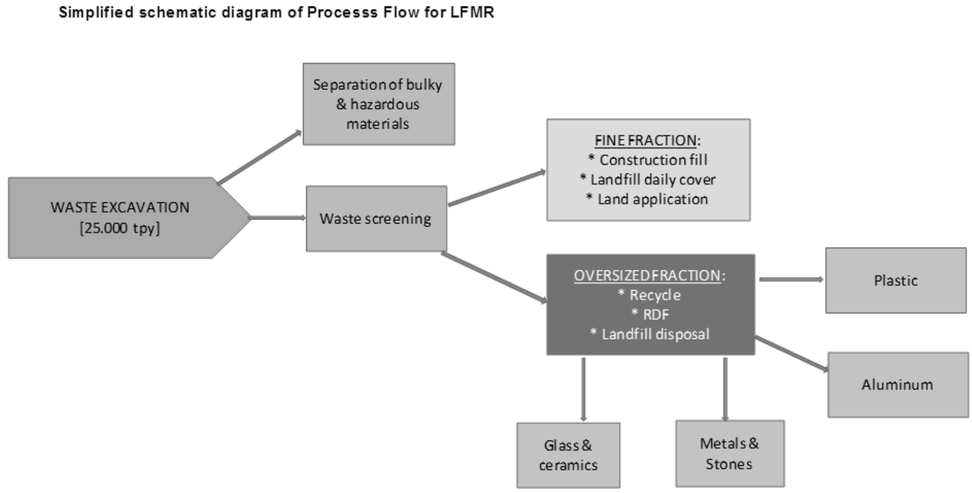


Figure 1. Simplified schematic diagram of Process Flow for LFMR

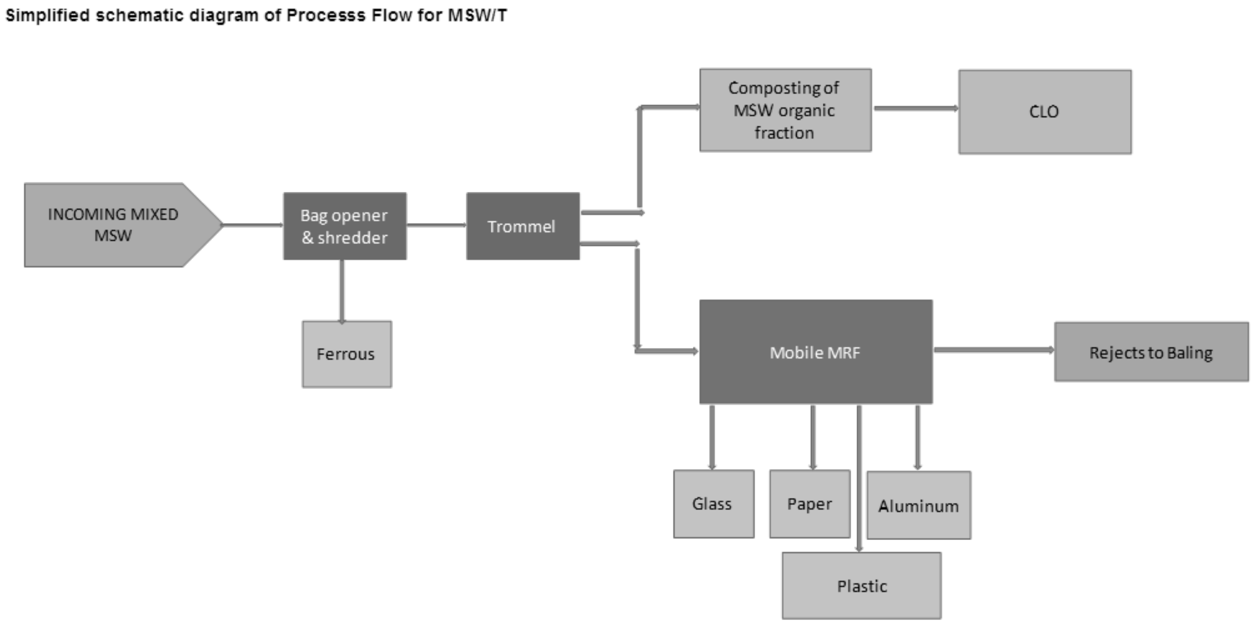


Figure 2. Stages of mixed incoming Municipal Solid Waste Treatment

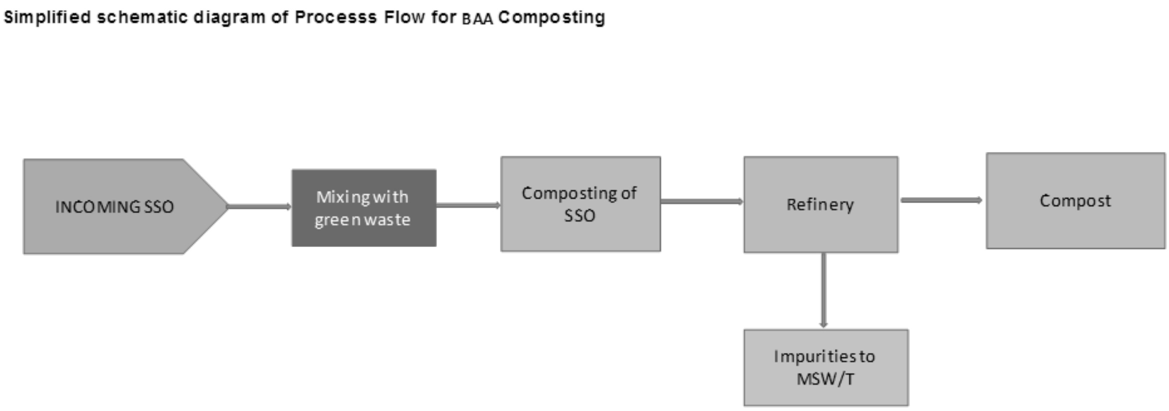


Figure 3. Composting of Source Separated Organics (SSO)

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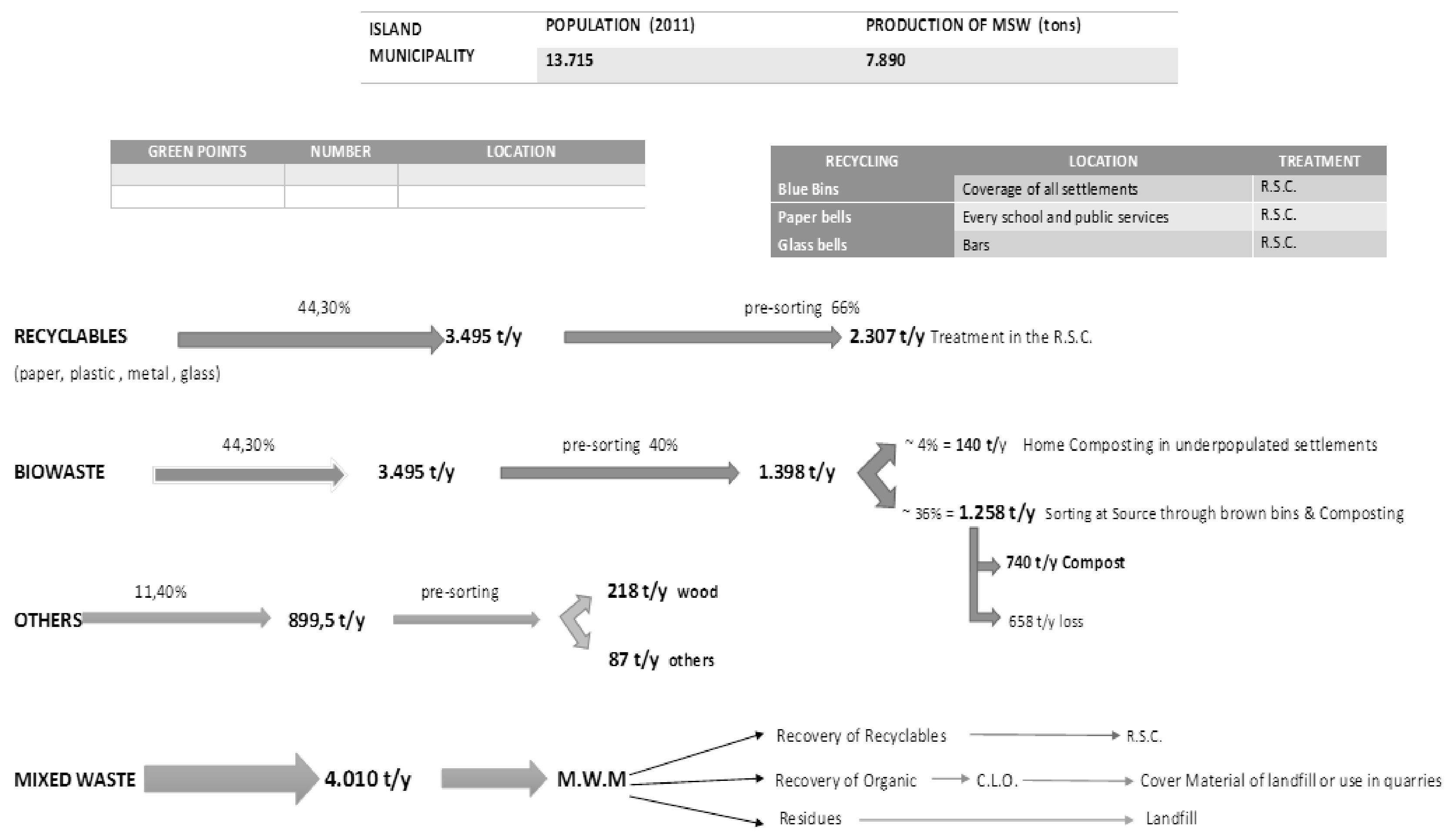


Figure 4: Mass balance of MSW Processing and Treatment

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4. COST ANALYSIS OF $MSW/T\ \sqrt{LFMR}$SYSTEM

The structure of both the Capital (Capex) and Operational Expenditure (Opex) of the system is presented in the Table below. It is to be mentioned that the figures below have been taken from similar projects, while the detailed analysis of Capex and Opex will arise as the outcome of the system operation, after its implementation.

Table 1. Cost Analysis of the Landfill Mining & Reclamation (LFMR) Mobile Unit

UNIT 1st: LANDFILL MINING (LFMR)	**Price (€)**	**Quantity**	**Total (€)**
Excavator	180.000	1	180.000
Trommel	200.000	1	200.000
Conveyor belts	20.000	1	20.000
Magnetic Separators	60.000	1	60.000
Other infrastructure	30.000	1	30.000
		TOTAL CAPEX	*490.000*

The Operational Expenditure (Opex) for this Unit is estimated to 10-15€/ton of excavated material, while the Capex will be 100% publicly funded.

Regarding the Revenues from this kind of operation, it is to be noted that we are expecting two basic streams of it:

- Direct revenues: This is due to the recovery of sellable materials such as Fe, Al and plastics. It is expected that these materials can constitute 5-6% of the excavated waste.
- Indirect revenues: This type of revenues will come from two main sources:
    a. Restoration avoidance: According to such a typical study, the total cost of this dumpsite restoration is approximately 450.000 Euros.
    b. New LS avoidance: This represents a serious indirect cost. Based on the experience as per the operation of other LS in the country the weighed value of a new LS with the use of cover material is anticipated to 20-30.000€/yr.

It is therefore anticipated that the final revenues, especially the indirect ones, will finally overcome the cost of setting up and running the Project, thus making the implementation of it quite attractive.

Table 2. Cost Analysis of fresh MSW Treatment (MSW/T) Unit

UNIT 2nd: MSW TREATMENT (MSW/T)	Price (€)	Quantity	Total (€)
Weighbridge, office	20.000	1	20.000
Mobile Sorting Line	65.000	1	65.000
Compact unit for leachate treatment	40.000	1	40.000
Bag opener	175.000	1	175.000
Trommel	185.000	1	150.000
Composting Unit	150.000	1	150.000
TOTAL CAPEX			600.000

The Operational Expenditure (Opex) for this Unit is estimated to 25-30€/ton of incoming mixed MSW, while Capex will be (as in the previous Unit) 100% publicly funded.

It is but to be noted that, according to the legislation, for every ton of untreated MSW that is landfilled a «landfill tax» is allowed that is up to 35€. The annual increase of this tax is 5€/ton climbing up to a final rate of 55€/ton.

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Based on this, it is obvious that the goal of a mobile MSW/T Unit, like the one described, is twofold:

- It complies with the set recycling and biodegradable waste diversion rate.
- It successfully compares to the set landfill tax.

As a result, the analysis shows that the combined Units (LFMR & MSW/T) not only can contribute in solving a long lasting problem of environmentally sound MSW Management but also the logistics are such that it makes the system economically sound.

5. CONCLUSIONS

This paper presents an integrated Solid Waste Management solution that combines Landfill Mining & Reclamation Principle with of MSW Treatment. The above model is suitable for application in many places in Greece, especially in Islands, while at the same time Source Separation of Packaging materials and Organic Waste must meet certain, time framed, goals.

The typical remediation process of a dumpsite is expensive and does not promote Land Reclamation and Resource Recovery. On the other hand, Landfill Mining & Reclamation process is a more cost-efficient solution, comparing to typical remediation measures, while converting already used area in the LS to clean area suitable for future Landfilling Operation.

Additionally to this, LFMR process in combination with fresh MSW Treatment:

a. Strengthens materials' recovery and recycling.
b. Contributes to the local economic development through Resource Revenues and Real estate.
c. Minimises the waste that need to be finally disposed of in a landfill.
d. Meets the National goals of Recycling and Biodegradable diversion rates.

Therefore the above described approach can be defined as a MODEL that should be promoted and adopted by small to medium islands in Greece.

References

[1] Cossu, R., Hogland, W., Salerni, E., (1996). *Landfill mining in Europe and the USA*. ISWA Year Book 1996, 107-114.

[2] Ford, S., Warren K., Lorton, C., Smithers, R., Read, A. and Hudgins, M. (2013). *Feasibility and Viability of Landfill Mining and Reclamation in Scotland, Scoping Study, Final Report*, Zero Waste Scotland.

[3] Frantzis I. et al. (2015). *Feasibility study of LFMR in the Landfill Site of Volos*, Greece.

[4] Frantzis, I., Dareioti, M., Skoura, D., (2016). *Technical Support for the Implementation of LFMR and MSW/T in Messini Municipality*.

[5] Gaitanarou, Z., Tentes, G., Katselis, Y., (2012). *Landfill Mining: An empirical review on past and state-of-the-art applications*.

[6] Hogland, W., Hogland, M., Marques, M., (2011). *Enhanced Landfill Mining: Material Recovery, energy utilization and Economics in the EU (Directive) perspective*.

[7] Hogland, W., Hogland, M.,Kriipsalu, M., Kaczala, F., Bhatnagar, A.,(2012). *Closing the Life Cycle of Landfills-Landfill Mining in the Baltic Sea Region for future*.

[8] Krook, J., Svensson, N., Eklund, M., Johansson, N., Frandegard, Per.,(2010). *Landfill Mining: A Review of three decades of research*

[9] Kurian Joseph, Esakku,S., Palanivelu,K., and Selvam A. (2003). *Studies on Landfill Mining at Solid Waste Dumpsites in India*, Procs. Sardinia 2003, Ninth International Waste Management and Landfill Symposium, Cagliari, Italy, 6-10 October.

[10] Rosendal R. M., (2009). *Landfill Mining: Process, Feasibility, Economy, Benefits and Limitations*

[11] USEPA (1997). "*Landfill Reclamation*, United States Environmental Protection Agency (EPA), Report No.EPA530-F-97-001.

[12] Van der Zee D.J. Achterkamp, M.C., De Visser B.J. (2004). *Assessing the opportunities of Landfill Mining.*

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Modified contingent valuation method for agricultural wastes between the area of Peloponnese and Thessaly in Greece

O. N. Kopsidas[1*], A. N. Kopsidas[2]

[1] Department of Civil Engineering, Alexander Technological Institute of Thessaloniki, Sindos Thessaloniki, Greece.
[2] School of Civil Engineering National Technical University of Athens, Heroon Polytechneiou 9, 157 80 Zografos – Athens, Greece.
*Corresponding author: Email: odykopsi@yahoo.gr

Abstract

This paper focuses on investigating the tendency of farmers in the greater area of Peloponnese as well as those on the greater area of Thessaly to participate in a program of environmental agricultural waste management. The aim of the present study is to investigate the level of amount Willingness to Accept (WtA) against which the farmers would be willing to allow anyone to gather and carry away the leftovers of their farming exploitation. To serve the above goals, the agricultural leftovers are evaluated by the Contingent Valuation Method (CVM) as an environmental non-market economic commodity. The specimen response on utilization of the rejected biomass was satisfactory, since a good percentage of the interviewees are willing to contribute to this procedure for a minimal of remuneration, although investigations of this type are novel for Greek reality. From this investigation it is perceived by the society the importance of alternative utilization of the rejected biomass. We conclude that the minimum amount each interviewee is willing to accept as minimal remuneration, is affected by the way these biomass leftovers are managed, the age of the interviewees and the area in which they live. Those interviewees who use such biomass leftovers in alternative applications wish to be remunerated higher compared to those who relinquish such leftovers. The ordinal logistic model is listed in a broader category of Generalized Linear Models for arrangement data.

Keywords: *Willingness to Accept; WTA; biomass; ordinal model; parametric approach; questionnaire, interviewees, public good, external cost, environmental protection, non-market resources*

1. INTRODUCTION

The Contingent Valuation Method (CVM) is a survey-based technique, frequently used in Experimental Economics, especially useful for the valuation of non-market resources/goods/ services, and cultural heritage objects (of aesthetic, historic, scientific or social value), such as conservation of monumental remains and preservation of the physical and anthropogenic environment [1-2]. The basic partial techniques used in CVM are (i) willingness to pay (WTP), which is the maximum monetary amount that an individual would pay to obtain/preserve a good, and (ii) willingness to accept (WTA) compensation, which is the minimum monetary amount required to relinquish the good. Therefore, WTP provides a purchase price, relevant for valuing the proposed gain of the good while WTA provides a selling price, relevant for valuing the proposed loss of the good. According to classic economic theory, a significant difference between WTP and WTA should not occur, on condition that there is (i) no transaction cost, (ii) perfect information about goods/services and corresponding prices, (iii) no income effect, (iv) a market that engenders truthful revelation of preferences. Although these conditions were generally met in several

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economic experiments that used inexpensive market goods with readily available substitutes, the ratios WTA/WTP obtained were significantly greater that unity. This result was attributed to the fact that participants in these experiments lacked market experience [3].Contingent Valuation Method is the first technique of hypothetical experiments using a questionnaire applied to assess the economic value of public goods and services and is the predominant assessment technique in the scientific field of Experimental Economics.

The economic value of natural resources is often defined as the value of the goods and the services they offer. The environment economics have developed a series of methods for assessment of the monetary price of the environmental goods and services, which are based on investigation of the public preferences and reflect the practical need of translation of the monetary amount into management policies, in which the public concession and participation in the process of decision making are indispensable.

By the term Biomass we mean the biodegradable products fraction, wastes and leftovers coming from agricultural, plants and animal substances inclusive, the forestall and the like industrial plant, as well as the biodegradable fraction of industrial wastes and urban effluents and sewage wastes.

2. IMPLEMENTATION

We compare the results of the descriptive statistical analysis among the answers of the interviewees in the mainland Greece (Thessaly) and on Peloponnese. The similarities and differences in the attitude of these two categories of rural population are outlined. We observe that the interviewees in the previous year owned bigger areas of land (more stremmas) per cultivated item on Peloponnese compared to Thessaly. Also the interviewees stated that they had almost the same number of stremmas against the average stremmas owned by the farmers in Thessaly, on Peloponnese. Most of the interviewees in Thessaly utilize the crop leftovers in other applications but on Peloponnese gather it for fuel at home. It is worth noting that management of the rejected biomass does not differ among the above areas.

On the contrary, however, we notice that the minimum compensation amount each interviewee asks in order they may be in a position to gather and carry away the leftovers differs among the areas. More specifically on Peloponnese the farmers ask for higher remuneration compared to farmers in the Thessaly area. However, the willingness shown by the farmers for participation in gathering the crops without any extra remuneration does not differ among the areas.

As regards the income of each interviewee farmer against that of inhabitants in other areas of similar agricultural exploitation it does not differ between the two area categories, as the results show. Additionally we notice that the percentage of the interviewees' income originating in farming is bigger in Thessaly compared to that on Peloponnese. In order we correlate the amount WTA with the rest of the parameters of our example, we apply the model «ordinal regression», given that the dependent variable (WTA)is scaled and the independent variables are discreet (nominal or scaled).
We conclude that the minimum amount each interviewee is willing to accept as minimal remuneration, is affected by the way these biomass leftovers are managed, the age of the interviewees and the area in which they live. Those interviewees who use such biomass leftovers in alternative applications wish to be remunerated higher compared to those who relinquish such leftovers.

The interviewees aged 15 to 25 years wish to be remunerated with smaller amounts compared to those aged 56 up (p-value=0,045<0,05). Further, we notice that the farmers aged 26 to 40 years wish to be remunerated with higher amounts compared to those of 56 years up (p-value=0,018<0,05). Finally, the interviewees in the Thessaly area wish to be remunerated with smaller amounts compared to those on the islands of Peloponnese.

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The ordinal logistic model listed in a broader category of Generalized Linear Models for arrangement data. The model is based on the assumption that a latent continuous outcome variable exists and that the observed ordinal outcome results from the continuous discreteness of that subjected to j scaled groups.

The specimen of generalized linear models is given here:

$$\text{link}(\gamma_j) = \frac{\theta_j - [\beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_k x_k]}{\exp(\tau_1 z_1 + \tau_2 z_2 + \ldots + \tau_m z_m)} \quad \textbf{(1)}$$

where:

γ_i : cumulative possibility for category j

θ_j: threshold of category j

$\beta_1 \ldots \beta_\kappa$: reciprocation coefficients

$\chi_1 \ldots \chi_\kappa$: predictor variables

κ: number of predictions

The specimen numerator determines the location of the model while the denominator determines the scale. The terms $\tau_1..\tau_m$ are coefficients for the scale components while the terms $Z_1 \ldots Z_m$ represent the m predictor variables for the scaled components. The scaled components are the cause of differences in the variable of different values of the predictor variables.

The question formulates the Willingness to Accept (WtA) of the interviewee that is their wish for remuneration in order to allow someone to gather and take away the leftovers of the agricultural exploitation. It is impressive that the majority of the interviewees, i.e.71.7% of the specimen, answered that they would relinquish their farming leftovers without asking for any monetary remuneration. Out of the remaining 28.3% of the specimen, 11.7% answered that they would ask for 1-5 euro to relinquish the farming leftovers in each cultivated stremma on a yearly basis. Similarly another 11.7% of the specimen answered that they would ask for 6-10 euro for the same above reason. Finally, one person in each category(1,67% of the specimen), answered that the remuneration he would ask to relinquish his farming leftovers would be 11 – 15 euro in the first instance, 16 – 20 euro in the second instance and 21 euro up in the last instance.

We observe that in the first category , that is the one of those stating that they do not ask for any remuneration to relinquish their farming leftovers, 58.1% of the specimen would participate without any recompense in the entire process, while 41.8% would not participate without recompense.

In the second category, that is the one of those wishing to collect monetary remuneration to relinquish their farming leftovers, 47% of the specimen answered that they would participate in the relevant procedure, contrary to the 52.9% of the interviewees who stated that they would not participate.

In the first category, i.e. those who stated that they do not wish any remuneration to relinquish their farming leftovers, 58.1% of the specimen would participate in the whole procedure without recompense while 41.8% would not participate without recompense.

In the second category, i.e. those wishing to collect monetary remuneration to relinquish their farming leftovers, 47% of the specimen answered that they would participate in the relevant procedure, but 52.9% of the interviewees stated that they would not participate.

Out of the first category which concerns those not wishing remuneration to relinquish their farming leftovers, 26% of the specimen stated that they abandon their farming leftovers in the field. An equal percentage (26%) states that they burn the leftovers in the field. Only 2.3% gather the leftovers as fuel at home while, finally, the majority that totals 45.2% mention utilization.

Out of the second category, which concerns those wishing remuneration to relinquish their farming leftovers, 26% of the specimen stated that they abandon the leftovers of their farming exploitation in the field.

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Out of the first category, i.e. those stating that they do not wish any remuneration to relinquish their farming leftovers, 18.6% of the specimen report an income smaller of the average of the farmers in the area who are involved in similar farming exploitation, 67.4% of the specimen report an income approximately equal to the average and finally only 13.9% of the interviewees report an income bigger than the average in the area.

Out of the second category, that is the one wishing to collect monetary remuneration to relinquish their farming leftovers, 23.5% of the specimen report an income smaller than the average of the farmers in the area with similar farming exploitation, 47% of the specimen report an income approximately equal to that of the average and finally only 29.41% of the interviewee report an income bigger than the average in the area.

$$R^2 = 1 - \frac{\sum_{i=1}^{N} \left(y_i - \hat{y}_i\right)^2}{\sum_{i=1}^{N} \left(y_i - \bar{y}\right)^2} \tag{2}$$

Where N is the number of observations, y is the dependent variable, $\bar{y}$ is the mean of the y values, and $\hat{y}$ is the value predicted by the model. R^2 is the determination coefficient that ranges from 0 to 1. According to the Ephron's R^2:

$$R^2 = 1 - \frac{\sum_{i=1}^{N} \left(y_i - \hat{\pi}_i\right)^2}{\sum_{i=1}^{N} \left(y_i - \bar{y}\right)^2} \tag{3}$$

where $\hat{\pi}$ =model predicted probabilities, the dependent variable in a logistic regression is not continuous while the predicted value (a probability) is. Mac Fadden introduced the log likelihood of the intercept model.

$$R^2 = 1 - \frac{\ln \hat{L}\left(M_{Full}\right)}{\ln \hat{L}\left(M_{Intercept}\right)} \tag{4}$$

$$2\ln\left[L\left(M_{Intercept}\right)/L\left(M_{Full}\right)\right] \tag{5}$$

Where Mc Full is the model with predictors, M Intercept is the model without predictors, and $\hat{L}$ is the estimated likelihood. A likelihood falls between 0 and 1, so the log of likelihood is less than, or equal to, zero. If a model has a very low likelihood, then the log of the likelihood will have a larger magnitude than the log of a more likely model. Cox and Snell present the R^2 as a transformation of the Statistic that is used to determine the convergence of a logistic regression.

$$R^2 = 1 - \left\{\frac{L\left(M_{Intercept}\right)}{L\left(M_{Full}\right)}\right\}^{\frac{2}{N}} \tag{6}$$

Note that Cox & Snell's pseudo-R^2 has a maximum value that is not 1; if the full model predicts the outcome perfectly and has a likelihood of 1, and then we have

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$$1-L\left(M_{Intercept}\right)^{\frac{2}{N}}<1 \qquad (7)$$

Nagelkerke, Cragg and Uhler, adjust Cox & Snell's R^2 so that the range of possible values extends to 1.

$$R^2=\frac{1-\left\{\frac{L\left(M_{Intercept}\right)}{L\left(M_{Full}\right)}\right\}^{\frac{2}{N}}}{1-L\left(M_{Intercept}\right)^{\frac{2}{N}}} \qquad (8)$$

It should be noted that adjustment of the model is considered good by the coefficient Cox and Snell=0,656 and the coefficient Nagelkerke = 0,683.

3. CONCLUSION

External effects are observed when supply or demand impose costs or confer a benefit to others. More specifically, the external effect is the impact of the behaviour of a producer or consumer well-being of another, which is not reflected in market transactions.

The economic evaluation of research aimed at improving overall social welfare. As an initial test for social welfare, the criterion used Pareto, under which a fully competitive market, an action or policy is socially desirable if it improves the position of all the individuals composing the society or at least some (weak criterion Pareto), but difficult position of any other (a strong criterion Pareto).Some benefits from the research are as follows: He offered a variety of options that allow the construction of statistical models capable. The number of interviews and the survey costs are lower compared to those required for investigations manifested preferences. However indicated drawbacks, such as the fact that: there was a bias due to discrepancies between stated intentions and actual behaviour of interviewees.

The specimen response on utilization of the rejected biomass was satisfactory, since a good percentage of the interviewees are willing to contribute to this procedure for a minimal of remuneration, although investigations of this type are novel for Greek reality. From this investigation it is perceived by the society the importance of alternative utilization of the rejected biomass.

It is impressive that the majority of the interviewees, i.e. 43 persons who represent 71.7% of the specimen answered that they would allow their gathering and carrying away of their farming leftovers without asking for any monetary remuneration. Further, encouraging are the results concerning the willingness to participate in the gathering since the majority of the interviewees, i.e. 55% of the specimen, stated that they would participate in the gathering of the leftovers without any remuneration.

With regard to the amount WTA (dependent variable) of the Logit model we conclude that it is affected by the wish for remuneration (independent variable) at the level of importance 5% (p-value = 0.011). We also conclude that the amount of WTA is affected by the stremmas each farmer owns compared to other farmers at the level of importance 10% (p-value = 0.065).

References

[1] Brown,T.C., Loss aversion without the endowment effect, and other explanations for the WTA–WTP disparity, J. Econ. Behav.Org., 57, 367-379 (2005.

[2] Batzias,F., O. Kopsidas, Introducing a conditional 'Willingness to Pay' index as a quantifier for environmental impact assessment, 8th Int. Conf. Comput. Methods Sci. Eng., Kos, Greece, 2010, Amer. Inst. Physics.

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[3] Liao,T.F., Interpreting Probability Models: Logit, Probit, and other Generalized Linear Models. SAGE Publications Inc., 1994.
[4] Menard,S., Applied Logistic Regression Analysis, 2nd ed., SAGE Publications Inc., 2001.
[5] Rayleigh,L., Proc Roy. Soc. London 66, 68,1899-1900.
[6] Rayleigh,L., Nature 95,66 (1915).
[7] Buckingham,E., Phys. Rev.,4, 345-376,1914.
[8] Langahaar,H.E., Dimensional Analysis, London, 1951.
[9] Huntley H.E., Dimensional Analysis, London, MacDonald,1952.
[10] Palacios,J.,(translated by P. Lee with L.Roth), Dimensional Analysis, London, Mac Millan, 1964 (originally published in Spanish,1956.
[11] Allais M.,Traite d' economie pure, Vol. I, Les Donnees generals de l' economiepure , Paris and vol. IV, Annexes (2nd Ed. of a textbook published in 1943 under the title A la recherché d'une discipline economique.
[12] Jong,F.J. Dimensional Analysis for Economists, Amsterdam, North Holland Publ. Co,1967.
[13] Boulding,K.E., Economic Analysis, 4th Ed., Vol. II, New York, 1966.
[14] Auckley,G., Macroeconomic Theory, New York, 1961.
[15] Walker,G.M., L.R. Weatherley, J. Chem. Eng. 83, 201-206, 2001.

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Slag use in road construction acts favorably for the environment

A. Athanasopoulou*, G. Kollaros

Department of Civil Engineering, Democritus University of Thrace, 67132, Xanthi, Greece.
*Corresponding author: Email: anatha@civil.duth.gr

Abstract

The types of slag vary according to their chemical composition, their porosity and specific weight. This is due to the variability of coal and other materials initially used and to the cooling speed as well. This lack of uniformity does not exist only between slags from different sources, but even in the same furnace and among its different loadings. Samples of Greek slags have been tested in the laboratory. Tests of hardness and durability have been performed in order to define the engineering properties and characterize the material for use in pavement construction. The objective of this research was to determine if it physically makes sense to use slag in pavement and to understand the environmental implications which include reducing virgin materials thus yielding energy savings. The results have been compared with outputs for conventional aggregates. Synthetic aggregates can be used improving the costs of road products while they have mild impacts on the environment.

Keywords: slag; by-product; aggregate; road construction; environmental impact

1. INTRODUCTION

Generally, "slag" defines the main by-product of metallurgical industries. The most common metals for slag production are iron, steel, and nonferrous metals, like copper and nickel. Different methods are employed to cool the molten slag for disposal or use (air, pelletized, foamed, or granulated). It has been confirmed [1, 2, 3] there is a strong influence of steel slag on mechanical properties and durability of concrete towards to the improvement of the compressive and split tensile strength, both being much higher than that with limestone. Building up road pavement layers involve the use of large quantities of raw materials (cement, asphalt and aggregates), the production of which is associated to energy consumption and to the production of gas pollutants in substantial quantities. Many indications [4, 5] advocate that steel slag could be used as an aggregate for road construction. Utilization of steel slag as aggregate in asphalt mixture has been reported [6, 7]. Slags can be characterised as sustainable materials because they are easily recycled and could be reused in different applications. Valuable natural resources are saved when slags are selected as pavement aggregates while at the same time green house gases are reduced [4].

The suitability of copper, zinc, and steel slags (waste materials) as fine aggregate in road pavement structures (base and bituminous layers) has been investigated [8] in terms of their physical, chemical and geotechnical properties. An effort has been made to ensure the stability of steel slag and to judge its feasibility as an aggregate to prepare stone mastic asphalt (SMA) mixtures, due to its porous structure [9, 10]. A comparison to mixtures with basalt aggregate employing X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as mercury intrusion porosimetry (MIP) has shown a higher resistance of steel slag to permanent deformation at high temperature.

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The research presented here aimed to determine whether it physically makes sense to use slag in pavement layers (pavement quality concrete, cement bound road-base or other layers, bitumen bound layers, unbound subbase, capping, or general fill) and to understand the environmental implications which include reduction of virgin materials use, thus yielding cost and energy savings.

2. USE OF SLAGS IN ROAD CONSTRUCTION

Alternative materials are used in road construction in many countries in the developed world, but implementation varies due to the different chemical composition of materials and the way the production in each country. The specificities of the alternative material used in the construction of roads, should be taken into account, after laboratory testing for the determination of the properties of the material for successful applications. In Greece, alternative materials produced in sufficient quantities are: (a) slags (metallurgical, blast furnace), (b) fly ash from power stations, (c) bauxite byproducts (bauxite aggregates, limestone aggregates and red mud) (d) quarrying products (dunites, magnesite, marble).

Today, the use of alternative products as aggregates in road construction projects is a research and application field in the context of sustainable development. The metallurgical by-products, such as slag from the first and second ore-processing, are included in the hazardous wastes listed in 50910/2727/2003 joint ministerial decision (JMD) while their management is determined by the 13588/725/2006 JMD modified by the law 4042/2012 in line with the relevant directive 2008/98/EC. Nevertheless, the law does not specify environmental requirements for the use of slag as aggregate in road construction projects; their suitability is evaluated based on their engineering characteristics. The ASTM D 5106-15 [11] specification includes further engineering requirements and criteria for toxicity under the TCLP (Toxicity Characterization Leaching Procedure) test [12].

The steelworks and steel processing enterprises in Europe have been under the constitution of EUROSLAG. Starting from 2000 and in biennial intervals surveys are conducted among EUROSLAG members. The purpose of these surveys is to access different types of slags in view of their importance, as well as to critically summarize the characteristics of products manufacture using slag. Some results of surveys conducted in the past are given in Table 1 for steel slag and bottom furnace slag produced in 16 European countries.

Table 1. Uses of blast furnace slag (BF) and steel slag (SS) in Europe (in million tones)

Slag use	Year													
	2000		2002		2004		2006		2008		2010		2012	
	BF	SS	BF	SS	BF	SS	BF	SS	BF	SS	BF	SS	BF	SS
Road construction	11,6	6,6	10,0	6,8	8,9	6,8	10,6	11,9	8,2	10,7	5,9	10,7	6,6	10,6
Cement / concrete	16,4	1,3	14,2	1,4	17,4	0,2	21,3	0,3	21,8	0,2	16,9	1,3	16,6	1,2
Internal metallurgical		2,4		2,4		2,1		2,5		1,4		2,2		2,7
Hydraulic engineering	0,1	0,7	0,1	0,3	0,1	0,5		0,6		0,2		0,7		0,7
Fertilizers	0,1	0,7	0,1	0,7	0,1	0,5		0,6		0,7		0,7		0,7
Interim storage	0,8	1,2		1,2		2,6		3,4		2,6	2,6	2,5	3,9	4,7
Final disposal		4,0		4,1		1,7		1,6		1,0		2,9		3,2
Other	0,5		0,4		0,5	0,9	0,3	0,6	0,3	0,5	0,3	1,3	0,6	0,7

The blast furnace slags consist of different types of product, namely: granulated, air cooled and pelletized. The contents differ from year to year. Steel slag is also a mixture of different kinds of products, i.e. basic oxygen furnace slag (BOS), electric arc furnace (EAF) slag (EAF-C, from

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carbon steel production and EAF-S, from stainless steel production.), and secondary metallurgical slag (SECS). In comparison with natural rocks, BOS has increased skid resistance and high impact and crushing values (high strength level). Thus, it could be used as aggregate and in road surface layers providing high skid resistance. EAF slag is characterized as non-porous aggregate having good resistance to polishing under loads. Its affinity to bitumen is excellent making it an ideal aggregate for materials placed as surfacing in road construction projects. At the same time EAF adds durability, resistance to rutting and hence safety to the surface of road pavements. SECS are mainly used as fertilizers, while some coarse grained are recycled in other processes of metallurgy.
In Figure 1, the steel slag quantities collectively counted in sixteen European countries are shown along the respective volumes of steel slag reclaimed in road construction, in million of tonnes. The data have been processed by the authors based on recorded values by the EUROSLAG Association.

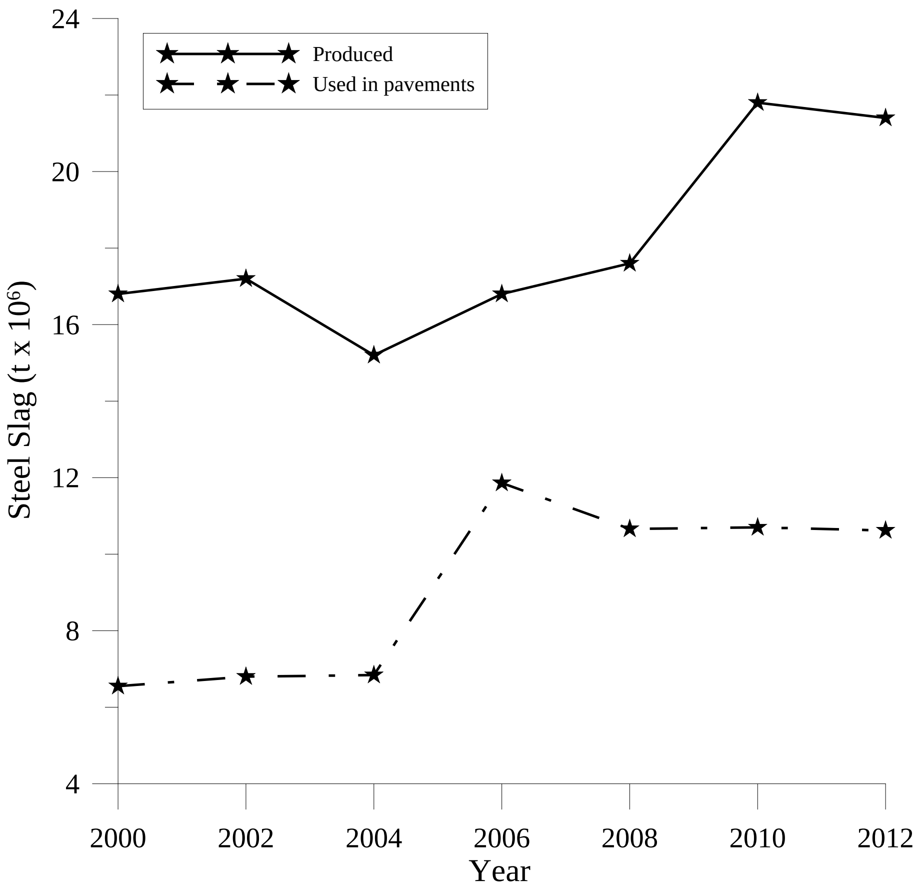


Figure 1. Annual production and use of steel slag in Europe

Industries producing slag products in Greece are Viohalko S.A. and its steel production and trading branch, Sidenor, in Thessaloniki (71,000 tones produced annually), HALYVOURGIKI, Hellenic Halyvourgia S.A. in Elefsina-Aspropyrgos (6,000 tones produced annually), general mining and metallurgical company LARCO S.A. in Larymna (1,500,000 tones produced annually), and Halyvourgia Thessalias, Metallourgiki Chalyps in Almyros near Volos.

Ensuring uses for all slags produced, the need to use natural resources is reduced. Therefore, no additional energy consumption is required for the production of raw materials with natural rock mining. Regarding the energy and material consumption, no official comparative quantitative data exist on the use of natural or artificial aggregates for the construction of anti-skid pavements. Also, no difference has been reported on how to use them, while during asphalt mix preparation and paving, no additional waste is generated by the use of slag aggregates. As the road construction aggregates are used in projects directly related to public health, all necessary checks have to be performed.

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The physical characteristics of aggregates derived from those of the raw material, i.e. the electric furnace slag, and are not altered during the manufacturing process or after their inclusion in anti-skid roadway pavements. Characteristic of the production process is the fact that no new waste is generated, since the total quantity produced is exploited. Also, at all stages dry processing is followed (aggregate crushing, separation, and gradation) and emissions in the atmosphere are within the limits set by the European Community. A research [13] on the slag exploitation possibilities in skid resistant pavements has been completed in 2005.

3. LABORATORY EXAMINATION OF GREEK STEEL SLAGS

It is recognized that steel slag is a material with high specific weight and it has a very good anti-skid resistance when used as an aggregate in pavement structures. On the other hand, steel slag is chemically stable and shows excellent binding properties with bituminous materials [14]. As a whole, steel slag has very good mechanical characteristics. The addition of steel slag in asphalt mixtures enhances the performance characteristics of pavement [15]. The skid resistance expressed via the British Pendulum Number (BPN) coefficient fits with an excellent performance of the surface layer at in service temperatures [16]. The stability and rutting resistance of the hot mix asphalt is increased because of the specific value of steel slag and the interlocking properties arising from the angular shape of the material. Road construction is characterized by the use of large quantities of aggregate materials. The aggregates market plays an important role in Greece's economy, since it constitutes 45% of total mineral mining (roughly 58 Mt annually). Their production supports the Greek economy, however the way of mining and production has important environmental impacts (gas pollutants, noise, dust, aesthetic nuisance).

In Greece, slag has already been used in road construction works. The main sites of such a use are located on the Attica motorway, the Egnatia motorway (Ardanio-Kipi, slurry seal), the Northern road axis in Crete and on the Patras-Athens-Thessaloniki-Evzoni (PAThE) motorway, namely in sections of the Skotina-Katerini, Yliki-Agios Konstantinos, Agioi Theodoroi-Almiros segments. Skid resistant surface layers (Type II) have been constructed on the Lamia-Karpenisi National Road, Aegean Motorway, and on local Thessaly highways like the Volos-Aghialos Provincial Road.

Samples of Greek slags from the steel industries in Lavrio and Larymna (S1 and S2 respectively) have been tested in the laboratory. Hardness and durability tests had been performed in order to define the engineering properties and characterize the material for use in pavement construction. For comparison reasons, the same laboratory controls have been executed on 68 different rock aggregates sampled in different regions all over Greece. The rock deposits consisted of basalts, gabbros, granites, sandstones, limestones, porphyries, quartzites, schists, and shingles.

Slag samples have been tested for their resistance to abrasion (Los Angeles, ASTM C131-96), and Polished Stone Value (PSV, BS 812:114-89) values. The two tests aim the determination of the gradate aggregates to wear under the effect of friction and impact forces and the aggregates' behaviour under the polishing action of vehicle tires. The results of both tests on S1 and S2 samples along with the test outputs of other Greek slags by different researches S3, S4, S5 [13] and S6 [17] are listed in Table 2. The laboratory test results verify that the Greek slags conform to the Greek guides. According to Greek specifications [18], the maximum allowable Los Angeles value is taken as 40%, when the intended use of aggregates is in base or subbase layers. For surface layer aggregates, the maximum Los Angeles values along with those of PSV and aggregate abrasion value (AAV) are shown in Table 3.

A comparison among laboratory determined features of the slags and sixty seven natural hard aggregates distributed in the islander and land country. The results of the Los Angeles test showed that all slags presented adequate resistance to abrasion and friction (Table 4). The Los Angeles coefficient was in all cases lower than the limit (30%) required by the Greek specifications.

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Sandstones and porphyries have shown the higher loss when the Los Angeles testing procedure was applied, while at the same time they have presented the higher variation in Los Angeles values, ranging from 16 to 41 and from 19 to 40, respectively.

PSV values recorded for the slags tested in the present research program were 51 and 62 for S1 and S2, respectively, being lower than the limit values posed by the Greek specifications. As shown in Table 4, limestone presented very low PSV values, compared to other natural aggregates.

Table 2. Slag engineering characteristics

Test Method	Standard	Slag Sample					
		S1	**S2**	**S3**	**S4**	**S5**	**S6**
Specific Gravity (Relative Density)	ASTM C127 – 12 Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate	3.2	3.0	3.352	3.465	3.241	3.3
Aggregate soundness	ASTM C88 – 13 Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate	0.20	0.80	0.50	1.20	0.12	0.13
Los Angeles	ASTM C131 – 14 Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine	23	21	16	18	29	15
PSV (Polished Stone Value)	BS812:114-89 for determination of the polished-stone value	51	62	61	66	45	64
Flakiness	BS812:115.1-89 particle shape, Flakiness index	19.3	18.7	16.7	14.5	22.0	21.8

Table 3. Greek technical guidelines concerning limit values for surface layers' hard aggregates Los Angeles, PSV, and AAV

Traffic Volume	**Low**	**Medium**	**Heavy**	**Very Heavy**
Daily volume per lane	≤500	501-3,000	3,001-8,000	>8,000
max fragmentation percentage by Los Angeles test	30%	28%	26%	24%
min PSV on site				
A - Dangerous	50	55	60	65
B - Standard	45	50	55	60
C - Easy	---	45	---	---
Max AAV	14	12	10	8

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Table 4. Laboratory Los Angeles and PSV values of natural aggregates and slags

Rock type	No. of Samples	Los Angeles	PSV
Basalts	7	16-32	45-65
Gabbros	15	17-22	49-56
Granites	8	21-22	50-58
Sandstones	6	16-41	54-67
Limestones	2	23-25	40-45
Porphyries	9	19-40	52-60
Quartzites	10	16-30	53-70
Schists	4	15-30	51-64
Shingles	6	18-28	47-67
Slags	6	15-29	45-66

CONCLUSIONS

The sustainable or viable management of natural resources requires the decoupling of economic growth, use of resources and the waste production. An answer to the high cost and the restrictions to waste types could be found to the community's ability to choose alternative uses for waste products nowadays remaining unexploited. Steel slag is a by-product of the steel industry exhibiting great potential as a replacement for natural aggregates in road construction. It is also a recyclable waste material which can be used as a road construction material. Slag has successfully replaced aggregates for hot mix asphalt, road base and subbase layers.

Industrial by-products are a challenging way of saving energy and protecting the environment. Criteria are needed for the mechanical behaviour of waste materials, especially slag, in pavement construction. For a complete design procedure, a proper quantification of samples is also needed.

Slags are suggested for industrial roads, intersections, and parking areas, because high wear resistance is required in such sites. The slags tested in the laboratory conform to Greek specifications and could play a role in the construction of pavement layers. The comparison to conventional materials has proved that the benefits from the use of specific slags produced in Greece, particularly near roadway construction sites, will enhanced the technical, environmental, economic and social features of highway works. Of course, reliable laboratory controls, extensive on-site evaluations, practical utilization in different projects and comprehensive research there remains to be performed in the near future.

References

[1] Maslehuddin, M., Sharif, A.M., Shameem, M., 2003. Comparison of properties of steel slag and crushed limestone aggregate concretes. *Construction and Building Materials*, **17**, 105 – 112.

[2] Beshr, H., Almusallam, A.A., Maslehuddin, M., 2003. Effect of coarse aggregate quality on the mechanical properties of high strength concrete. *Construction and Building Materials*, **17**, 97 – 103.

[3] Ysof, M.A.W., 2005. Investigating the potential for incorporating tin slag in road pavements. Ph.D. Thesis, University of Nottingham

[4] Motz, H., Geiseler, J, 2001. Products of steel slags an opportunity to save natural resources. *Journal of Waste Management*, **21(3),** 285 – 293.

[5] Aziz, M.M.A., Shokri, M., Ahsan, A. Liu, H.Y., Tay, L., Muslim, N.H., 2015. An overview on performance of steel slag in highway industry. *Journal of Advanced Review on Scientific Research*, **5(1)**, 30 – 41.

[6] Hainin, M.R., Yusoff, N.I., Sabri, M.F.M., Aziz, M.A.A., Hameed, M.A.S., Reshi, W.F., 2012. Steel slag as an aggregate replacement in Malaysian hot mix asphalt. *International Scholarly Research Network Civil Engineering*, 5 p.

ISBN: 978-960-6865-94-7

[7] I. Liapis, and S.Likoydis, 2012, Use of electric arc furnace slag in thin skid-resistant surfacing. *Procedia - Social and Behavioral Sciences*, **48**, 907 – 918.
[8] Havanagi, V.G., Sinha, A.K., Arora, V.K., Mathur, S., 2012.Waste materials for construction of road embankment and pavement layers. *International Journal of Environmental Engineering Research*, **1(2)**, 51 – 59.
[9] Wu, S., Xue, Y., Ye, Q., Chen, Y., 2007. Utilization of steel slag as aggregates for stone mastic asphalt (SMA) mixtures. *Building and Environment*, **42(7)**, 2580 – 2585.
[10] Hainin, M.R., Rusbintardjo, G., Aziz, M.A.A., Hamim, A., Yusoff, N.I.M., 2013. Laboratory evaluation on steel slag as aggregate replacement in stone mastic asphalt mixtures. *Jurnal Teknologi*, **65(2)**, 13 – 19.
[11] ASTM, 2015. ASTM D 5106-15 "*Standard specification for steel slag aggregates for bituminous paving mixtures*" ASTM International 2015.
[12] Tiwari, M.J., Bajpai, S., Dewangan, U.K., Tamrakar, R.K., 2015. Suitability of leaching test methods for fly ash and slag: A review. *Journal of Radiation Research and Applied Science*, **8(4)**, 523 – 537.
[13] Prapidis, A., Ntoulis, G., Zotiadis, B**,** 2005. Slag use in skid resistant asphalt mixtures based on engineering and environmental criteria. *Proceedings Heleco '05. Technical Chamber of Greece*, Athens, 8 p. (In Greek).
[14] Pasetto, M., Baldo, N., 2012. Performance comparative analysis of stone mastic asphalts with electric arc furnace steel slag: A laboratory evaluation. *Materials and Structures*. **45(3)**, 411 – 424.
[15] Behnood, A., Ameri, M., 2012. Experimental investigation of stone matrix asphalt mixtures containing steel slag. *Scientia Iranica*. **19(5),** 1214 – 1219.
[16] Wu, S., Xue, Y., Ye, Q., Chen, Y., 2007. Utilization of steel slag as aggregates for stone mastic asphalt (SMA) mixtures. *Building and Environment*. **42(7)**, 2580 – 2585.
[17] Economou, N., Eskioglou, P., 2005. Metallurgical slag use in the construction of skid resistant micro-surfacing. *Proceedings 1st Panhellenic Congress EVIPAR "Exploitation of industrial by-products in building"*, 439 – 447.
[18] Anastasiou, E., Papayianni, I., 2006. Criteria for the use of steel slag aggregates in concrete. *Measuring, Monitoring and Modelling Concrete Propertie*s. Dordrecht, The Netherlands: Springer (Konsta-Gdoutos M.S. ed.), 419 – 426.

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The seven paths of translation evaluation: A control mechanism of bilingual scientific texts translations

S. Christidou[1*], S. Kamaroudis[2]

[1] Department of Mechanical Engineering, University of Western Macedonia, 50 132, Kozani, Greece.
[2] Department of Primary Education, University of Western Macedonia, 53 100, Florina, Greece.
* Corresponding author: Email: schristidou@uowm.gr

Abstract

During our academic research studies we have developed a control mechanism for translation based on seven variables taken by the Belgian translatologist Dirk Delabastita and processed further more. With this paper we aim to implement the control mechanism for translation on the subjects of Solid Waste Management and Liquid Waste Mechanics using the academic texts of *Handbook of Solid Waste Management* and *Wastewater Engineering, Treatment and Reuse* in order to investigate the quality of translations in Greek. We will present indicatively a psychometric questionnaire from the first research conducted to the Telecommunications scientists as well as an abstract of the processing of the relevant indexes followed by an indicative processing of the Environmental Engineering academic field. This could be the first step in research for the field of Environmental Engineering Terminology.

Keywords: translation strategies; indexes; psychometric tests; technical translation; Environmental Engineering

1. INTRODUCTION

This paper is partly based on a thesis, published on the site of the *Greek National Documentation Centre* and analyzed the translators' behaviors as far as the Greek language use is concerned in the fields of linguistics and telecommunications. In particular, our research aimed at exploring the translation strategies employed by the translators throughout the translation process. It seeks to reveal whether various innovations in terminology translation have become widely accepted by the scientific community of chemical, mechanical and environmental engineering and to what extent, and if the existence of different translations provided by translators, causes the special scientists to eventually prefer foreign terms or their turned-into-Greek versions instead of a purely Greek equivalent term.

The tools used in the researches on which this paper is based were the thorough processing and contrastive analysis of indexes of terms and questionnaires. The data that came to light underwent both a qualitative and a quantitative analysis. The indexes of terms -originals and their translations- were examined in detail with the use of the translation strategies. The working languages of the thesis were Greek and English. The findings of the suggested research could prove to be useful in translators' training.

2. THEORETICAL FRAMEWORK

2.1 Translation as an object of translatology

For the needs of this paper translatology is quoted with a broader sense, even though the approach of Jean René Ladmiral [1] is considered purely translatological. This happens because he follows

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the via media of the various translation theories. One can understand that by the fact that he chooses to examine philosophical texts. Undeniably, philosophical texts are classified amongst literary and technical-scientific texts. In the framework of medium road, Jean René Ladmiral locates the following aspects of translational phenomenon: translational entropy or addition, translational transparency or darkening, cultural elevation or leveling, terminological consistency or ambiguity, linguistic appropriateness or distortion, interpretation or meta-codification. Actually, these are the translator's everlasting questions. The same theorist considers it impossible to give all-embracing and specific answers and he claims that the unique judgment factor is each text separately and its translation pair.

On the other edge, the one that focuses on the target language, lies Gideon Toury [2], who calls his views "target-oriented". Important are his remarks on the ambiguity of "literary translation" (in Greek, this has a dual meaning thus the translation of literature texts or the word-for-word translation) and the classification of translation in: *linguistically-motivated*, *textually-dominated*, and *literary* or *word-for-word translation*. We should mainly, though, highlight his comments on the existence of a cultural distance between source language and target language, reinforcing his view on the respect towards the target language.

Surely not "extremist" but also not a representative of the via media is Peter Newmark [3] [4]. One could claim that his views are the first ones to get closer to technical translation. Newmark, in general, believes that a translation theory can neither be universal nor can it turn a bad translator to a good one. It can definitely, though, reveal bad writing and bad translation and for what reason, and at the same time it can suggest basic principles and guidelines some of which can be rather contradictory. Then he draws a distinction between communicative and semantic translation. The former includes the translation of non literary texts and focuses on the reader and the target language. On the other hand, the latter includes the translation of literary texts and places emphasis on the source language and the source text viewing it from a morphological and a content point of view. Ultimately, he mentions the "small"—but actually "big"—problems of translation such as the translation of proper names, institutions, cultural meanings, metaphors—according to him the most significant—but also of the terms that until then were ignored by the various theories of translation.

The distinction of text types introduced by Peter Newmark is intensely extended as an analytical strategy by Katharina Reiss [5] and the typological approach which she represents. According to it, the success of the translation mainly depends on whether the translator is aware of the type of the original text and maintains the special features that condition it. The text types are grouped in three basic types: informative, expressive, and operative texts. Each one's characteristics are clearly depicted by their naming. The first type aims at conveying information, so consequently the translation focuses on the precise communication of the information content. The second type is featured by the existence of an artistic or aesthetic style and as a result the translation has to respect the special characteristics of the original's form. Finally, the third type aims at persuading or dissuading, that is cajoling the reader, and as a consequence the translator's job lies in achieving the same impact on the reader as the original.

At the description of the aforementioned features the concept of Skopos is innate, a concept that becomes the fundamental term of Christiane Nord's [6] translation theory, who continues the thinking of Katharina Reiss. Christiane Nord introduces the functionalist study and translation criticism by presenting the "Theory of Action" and the "Skopostheorie/Theory of Skopos". In the first case, translating is conceived as "Intentional" and "Interpersonal Interaction", while in the second case, the "intention" and the "aim (purpose, skopos)" of the original text are being studied as components of translation, along with the abiding relationship with the "intratextual coherence". Definitely the intratextual coherence is based on the morphosyntactic rules of the target language that guide the text syntax.

Werner Koller [7], comments on the multi-used concept of equivalence, placing emphasis on denotative equivalence, and spots translation strategies that consist of particular types of

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correspondence: one-to-one correspondence, one-to-many correspondence or diversification, many-to-one correspondence or neutralization, one-to-zero correspondence or blank, one-to-part correspondence.

Apparently the above views focus on the communicative dimension of the translator. The work of Basil Hatim and Ian Mason [8] is considered to be within this framework, as obviously manifested by its title. Moreover, they stress the communicative aspect of translation, consisting of six parameters which, in their opinion, the translator should take into account and research: (1) cohesion; (2) coherence; (3) intentionality; (4) situationality; (5) intertextuality; and (6) informativity. The first two parameters concern the purely verbal aspect of translation, that is on a morphosyntactic level, the third and fourth the social—in a broader sense—aspect, and the latter two the semantic.

Lots of theorists and researchers followed the functional and communicative study of translation. One of them is Dirk Delabastita [9], on whose work is based a significant part of the study and search of our translation tool as it is going to be presented below. One can just note that in this case despite the modern theoretical background the suggested typology derives from the ancient rhetorics. However, this is not something striking given the fact that the art of rhetorics has mainly—let not say only—a communicative character, as translation does. Furthermore, this happened with renowned success—naturally on a practical level—in the historical beginnings of translation, as described before.

2.2 Translation as an Object of Special Texts Studies

Special texts study could not possibly be omitted from this paper. By the term “special texts”, we generally refer to technical and scientific texts. According to Hann [10] contrary to other areas of translation, which allow certain individuality on the part of the linguist with regard to lexicology and style, technical translation is essentially a decision-making process involving selection of the correct target language rendering from a number of different, context-dependent alternatives. A good literary translator strives to produce a target version which is as elegant and readable as the original, but the technical translator’s main priorities are precision and comprehensibility.

The approach of Pierre Lerat [11] stands out when it comes to special text studies. In his treatise *Les langues spécialisées*, he dedicates a chapter to translation mostly insisting on issues related to “terminology of specialized languages (jargon)”. This does not mean that he overlooks the general condition of special texts translation, since he mentions the concept of collocation, which consists of three different perspectives, depending on the way of approach: *pragmatic*, *syntactic*, and *semantic*. Thus, Lerat concludes to the distinction amongst “communicative adequacy” (competence), syntagmatic combination, and conceptual connectivity. Regarding terminology, his argumentation as a whole aims at the formulation of guidelines for the creation of “more linguistic terminological data bases”. Nevertheless, he openly points out the terminology management problem a translator is faced with, especially when using bilingual or multilingual dictionaries or terminology databases. At this point, he discusses a crucial point worth mentioning that lies in a very representative phrase: “...in order to be scientific, special English cannot be anything less but English!” [11]. This means that in every case of scientific or special idiolect, one has to use the morphosyntactic rules typical of the language of this idiolect.

The latter view contradicts another important approach to the study of special texts developed in the Anglo-Saxon academic field. The main concept of this approach is “sublanguage”, having its own vocabulary as well as its own “specialized grammar”, i.e., with its own morphosyntactic rules. This last property is definitely not acceptable. There cannot be another grammar in the same language as if it were a different language! In any case, the development of this theory regarded the automatic text processing and we theorize that the reasons for that were the poor results out of full grammar use.

3. RESEARCH METHODOLOGY

3.1 Research through index study

3.1.1 Theoretical framework

The extensive analysis of indexes presented in this paper was based on the translation strategies developed by the Belgian translatologist Dirk Delabastita [9]. Delabastita based the development of his strategies on the techniques used by the ancient Latin rhetoricians, as they were explained by Heinrich Lausberg [12] in his extensive presentation of the figures of speech used by ancient Greek rhetoricians. These figures of speech were copied by the Latin rhetoricians, starting by Cicero. This typology includes the following translation strategies:

(1) Repetitio: The sign is formally reproduced in an identical manner;
(2) Adiectio: The sign is reproduced with a certain addition;
(3) Detractio: The reproduction is incomplete, it implies a reduction;
(4) Transmutatio: The components of the signs are repeated in a somewhat different internal order, there being an alteration of the sign's textual relations;
(5) Substitutio: The sign is replaced with an altogether different sign.

All the above refer to the lexical, semantic and morphosyntactic level. Hence there is a variant of detractio, where all the elements of the translation unit are erased. This case is considered a different strategy and is called (6) deletio (deletion).

Finally, Sofia Christidou [13] [14] proposed through her academic research studies a new term: (7) non-translation[1] for the following cases: (a) where the term is not translated, not even transliterated but appears as it is in the source language; (b) where only part of the term is translated (e.g., a compound term which consists of two terms and has its first part kept in the source language without transliteration while its second one is translated in the target language with the employment of one of the aforementioned strategies); (c) where a term from the original index is omitted from the Greek index; (d) where acronyms and proper names remain in the source language without transliteration; and (e) where the wrong employment of one of the aforementioned strategies leads to a mistake in the translation of a term.

The aforementioned typology served as the basis for the study of the terms which were first studied as they appear in the indexes and then processed as they appear in context within the texts. The recording of the terms was done in the alphabetical order of the index in the source language. Term variations, when they appeared, were mentioned under the same entry, even if they had been recorded originally in the book as different entries of the same index. This was done to present the terms in their entirety and, consequently, analyze them in every respect. If the Greek index contained extra terms that did not appear in the original index, those were recorded separately. The next step that follows is the explanation of the translation strategy employed, including comments on the translation process. Moreover, a lexicographic and bibliographic research was performed, and, where necessary, suggestions of more accurate translations were made. Finally a statistical recording of the frequency of appearance of the translation strategies is presented which helps us come to conclusions regarding the decision-making processes.

3.1.2 Index Processing

Index processing examples of environmental scientific textbooks [15] [16]:

[1] As regards the term non-translation, it may be a term used in the translation theory to distinguish what is and what is not translation. However, there is controversy between the academics as to the circumstances where this term is used. Based on the definition given by the European Society for Translation Studies (EST), the term can refer to fragments of source text preserved in the original language in the target text. Furthermore one of the subcategories classified as non translation is covered by the definition given in the dictionary *Translation Terminology* (Publications Mesogios, Athens, 2008) for the term "direct transfer".

English term	Greek term	Translational choice
1) Recycling loop (index, I13) →	1) -	1) Non translation
2) The recycling loop, 9.1, p. 310, figure 9.1	2) Ο βρόχος ανακύκλωσης, 9.0, σελ. 450, σχήμα 9.1	2) Transmutatio

Comments - proposals

1) Non translation of this particular term, on account of its absence from the Greek Index.
2) A Transmutatio occurs, through the shifting of the present participle "recycling" from the second position of the English term to the third position of the Greek term, while at the same time it is transformed to the compound noun "ανακύκλωσης".

English term	Greek term	Translational choice
1)Solid waste collection, trash chute system (index, I14) →	1)-–	1) Non translation
2a) Collection of solid waste 7.2, p. 209, header	2a) Αποκομιδή στερεών αποβλήτων, 7.2, σελ. 316, κεφαλίδα	2a) Substitutio
2b) … of a trash chute system 7.2, p. 209, figure 7.4	2β) … ενός συστήματος αγωγών, 7.2, σελ. 316, σχήμα 7.4	2b) Detractio

Comments - proposals

1) Non translation of this particular term, on account of its absence from the Greek Index.
2a) A Substitutio occurs, through the replacement of the noun "collection" with the Greek noun «Αποκομιδή», which means transport and disposal. Additionally, a Deletio of the proposition "of" takes place because it is replaced with the genitive case in the Greek language.
2b) A Detractio occurs, through the removal of the noun "trash", which subtracts information from the term. Additionally, a Transmutatio occurs, through the shifting of the noun "chute" from the fourth to the third place of the term. Finally, a Deletio of the proposition "of" takes place because it is replaced with the genitive case in the Greek language.

English term	Greek term	Translational choice
1) Materials recovery facility (MRF) (index, I9) →	1) Κέντρου διαλογής Ανακυκλώσιμων Υλικών (ευρετήριο, 31)	1) Substitutio
2) Materials recovery facility (MRF), 1.4, p.30, l.10	2) Κέντρου διαλογής Ανακυκλώσιμων Υλικών (ΚΔΑΥ, Materials recovery facility, MRF), 1.4, σελ. 31, γρ. 3-4	2) Adiectio

Comments - proposals

1) A Substitutio occurs, through the replacement of the noun "recovery" with the noun «διαλογής», which means selection or triage. Also, a Substitutio occurs, through the replacement of the noun "facility" with the noun «Κέντρου», which means center. Additionally, an Adiectio occurs, by adding the adjective "ανακυκλώσιμων", which adds information to the term. Moreover, a

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Transmutatio occurs, by shifting the noun “Materials” from the first to the fourth place of the term. Finally, a Deletio of the acronym “MRF” occurs.

2) An Adiectio occurs, by adding the whole term as well as the acronym in English in brackets, an indication that the translator is not sure about his translation option. Moreover, a Substitutio occurs, through the replacement of the noun “recovery” with the noun «διαλογής», which means selection or triage. Also, a Substitutio occurs, through the replacement of the noun “facility” with the noun «Κέντρου», which means center. Additionally, an Adiectio occurs, by adding the adjective “ανακυκλώσιμων”, which adds information to the Greek term. Moreover, a Transmutatio occurs, by shifting the noun “Materials” from the first to the fourth place of the term.

3.2 Questionnaire Research

3.2.1 Presentation and analysis of the questionnaires

Firstly a selection of terms is made that appear in the source texts which consists the basis of the questionnaire. These options are called "reference texts" and are placed in the first column of the table of the questionnaire. In the second column the "Proposal Papers" can be found, where the proposed terms appear in bold letters. In the third column two kinds of answers are placed. The first concerns the question whether the respondents have seen or heard such terms and is a YES / NO question. The second question concerns the semantic level, i.e. whether the whole proposal is scientifically true or not, and is a TRUE / FALSE statement. Finally, the respondents are asked to underline the term in the reference text, whose rendering they considered was the term in the proposal text. The questionnaire has a total of 4 rows with text pairs (reference and proposal text) containing the selected terms (3 rows with 3 terms, 1 row with 2 terms). The first series has terms with a turned-into-Greek interpretation, the second with a mixed interpretation (using the English and the Greek language), the third with a new interpretation (i.e. proposal by the author) and the fourth with an incorrect interpretation (i.e. interpretation with scientifically different meaning, and then a proposal by the supervisor) in a misleading role (distractor). It is a psychometric test for special skills in order to measure a specialized knowledge in mainly the language level with scientific parameters.

ΚΕΙΜΕΝΟ ΑΝΑΦΟΡΑΣ	ΚΕΙΜΕΝΟ ΠΡΟΤΑΣΗΣ	ΑΠΑΝΤΗΣΗ	
Παρατηρούμε ότι ένας φωρατής ο οποίος βασίζεται στο MAP κριτήριο και ένας άλλος ο οποίος βασίζεται στο ML κριτήριο παίρνουν τις ίδιες αποφάσεις όταν οι a priori πιθανότητες $P(S_m)$ είναι όλες ίσες, δηλαδή όταν τα σήματα $\{S_m\}$ είναι ισοπίθανα. (J.G. Proakis and M. Salehi, *Συστήματα Τηλεπικοινωνιών*, Μετάφραση-Επιμέλεια: Κ. Καρούμπαλος, Ε. Ζέρβας, Σ. Καραμπογιάς, Ε. Σαγκριώτης, Εθνικό & Καποδιστριακό Πανεπιστήμιο Αθηνών, 2002: σελ. 428)	Παρατηρούμε ότι ένας φωρατής ο οποίος βασίζεται στο **κριτήριο της Μέγιστης εκ των Υστέρων Πιθανότητας (ΜΥΠ)** και ένας άλλος ο οποίος βασίζεται στο **κριτήριο της Μέγιστης Πιθανοφάνειας (ΜΠ)** παίρνουν τις ίδιες αποφάσεις όταν οι **πρότερες πιθανότητες** $P(S_m)$ είναι όλες ίσες, δηλαδή όταν τα σήματα $\{S_m\}$ είναι ισοπίθανα. (Μετάφραση: Κ. Καρούμπαλος, Ε. Ζέρβας, Σ. Καραμπογιάς, Ε. Σαγκριώτης)	ΝΑΙ ☐ ☐ ☐ Σ	ΟΧΙ ☐ ☐ ☐ Λ

ΚΕΙΜΕΝΟ ΑΝΑΦΟΡΑΣ	ΚΕΙΜΕΝΟ ΠΡΟΤΑΣΗΣ	ΑΠΑΝΤΗΣΗ	
Αν ορίσουμε δύο συναρτήσεις των τυχαίων μεταβλητών X και Y ως Z=g(X,Y) και W=h(X,Y), τότε οι συνδυασμένες CDF και PDF των Z και W μπορούν να προσδιορισθούν άμεσα εφαρμόζοντας τον ορισμό της CDF. (J.G. Proakis and M. Salehi, *Συστήματα Τηλεπικοινωνιών*, Μετάφραση-Επιμέλεια: Κ. Καρούμπαλος, Ε. Ζέρβας, Σ. Καραμπογιάς, Ε. Σαγκριώτης, Εθνικό & Καποδιστριακό Πανεπιστήμιο Αθηνών, 2002: σελ. 176)	Έστω Z=g(X,Y) και W=h(X,Y) δύο συναρτήσεις των τυχαίων μεταβλητών X και Y. Η **Συνδετική Κατανομή Πιθανότητας (joint CDF)** και η **Συνδετική Κατανομή Πυκνότητας Πιθανότητας (joint PDF)** των Z και W προκύπτουν με εφαρμογή του γνωστού ορισμού της **Κατανομής Πιθανότητας (CDF)** **(Μετάφραση: Σ. Χρηστίδου)**	ΝΑΙ ☐ ☐ ☐ Σ	ΟΧΙ ☐ ☐ ☐ Λ

13th International Conference on Protection and Restoration of the Environment
Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
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ΚΕΙΜΕΝΟ ΑΝΑΦΟΡΑΣ	ΚΕΙΜΕΝΟ ΠΡΟΤΑΣΗΣ	ΑΠΑΝΤΗΣΗ	
Μια άλλη μέθοδος για την εκτίμηση της φάσης φέροντος φ από το λαμβανόμενο Μ-αδικό QAM σήμα είναι η χρήση του DFPLL. Η βασική ιδέα για το DFPLL είναι η εκτίμηση της φάσης του QAM σήματος σε κάθε περίοδο σηματοδοσίας και η αφαίρεση της φάσης διαμόρφωσης από το φέρον. (J.G. Proakis and M. Salehi, *Συστήματα Τηλεπικοινωνιών*, Μετάφραση-Επιμέλεια: Κ. Καρούμπαλος, Ε. Ζέρβας, Σ. Καραμπογιάς, Ε. Σαγκριώτης, Εθνικό & Καποδιστριακό Πανεπιστήμιο Αθηνών, 2002: σελ. 438)	Εναλλακτικά, η φάση φ του φέροντος σε λαμβανόμενο σήμα με Μ-αδική **ΟΔΠ διαμόρφωση** μπορεί να προσδιορισθεί χρησιμοποιώντας **PLL με Ανάδραση Απόφασης:** αρχικά, προσδιορίζεται η **φάση του ΟΔΠ σήματος** σε κάθε περίοδο σηματοδοσίας και στη συνέχεια αφαιρείται η φάση της διαμόρφωσης από τη φάση του φέροντος. (Μετάφραση: Σ. Χρηστίδου – Λ. Χρυσουλίδης)	ΝΑΙ ☐ ☐ ☐ Σ	ΟΧΙ ☐ ☐ ☐ Λ

ΚΕΙΜΕΝΟ ΑΝΑΦΟΡΑΣ	ΚΕΙΜΕΝΟ ΠΡΟΤΑΣΗΣ	ΑΠΑΝΤΗΣΗ	
Όταν τα PAM σήματα βασικής ζώνης διαμορφώνουν ένα φέρον, η βασική γεωμετρική αναπαράσταση των ψηφιακών PAM κυματομορφών σήματος παραμένει η ίδια. (J.G. Proakis and M. Salehi, *Συστήματα Τηλεπικοινωνιών*, Μετάφραση-Επιμέλεια: Κ. Καρούμπαλος, Ε. Ζέρβας, Σ. Καραμπογιάς, Ε. Σαγκριώτης, Εθνικό & Καποδιστριακό Πανεπιστήμιο Αθηνών, 2002: σελ. 392)	Όταν τα **σήματα βασικής ζώνης** με **Παλμο-Διαμόρφωση Πλάτους (ΠΔΠ)** διαμορφώνουν ένα φέρον, η **βασική γεωμετρική αναπαράσταση των ψηφιακών ΠΔΠ κυματομορφών σήματος** παραμένει η ίδια. (Μετάφραση: Δ. Χρυσουλίδης)	ΝΑΙ ☐ ☐ Σ	ΟΧΙ ☐ ☐ Λ

3.2.2 Presentation of findings

25 valid questionnaires were collected and the following results were derived:

Term recognition-identification-usage

The questionnaire contains a total of 11 terms in the proposal texts. In the turned-into-Greek interpretation text, term 1 was recognized by 15 subjects (60%), term 2 was recognized by 18 subjects (72%) and term 3 was recognized by 12 subjects (48%). In the joint interpretation text, the term 4 was recognized by 11 subjects (44%), term 5 was recognized of 11 subjects (44%) and term 6 recognized by 17 subjects (68%). In the new interpretation text, term 7 was recognized by 8 subjects (32%), term 8 was recognized by subjects (44%) and term 9 was recognized by 8 subjects (32%). Finally, in the false interpretation text, the term 10 was recognized by nine subjects (36%) and the term 11 was recognized by 8 subjects (32%).

Locating phrase correctness

The text with the Turned-into-Greek interpretation was considered to be correct by 19 subjects (76%), while 4 subjects did not respond (16%). The text with the joint interpretation was considered to be correct by 12 subjects (48%), while 6 subjects did not respond (24%). The text with the new interpretation was considered to be correct by 17 subjects (68%), while 5 subjects did not answer (20%). Finally, the text with the false interpretation was considered to be correct by 18 subjects (72%), while 5 subjects did not answer (20%).

Correct term localization

For the turned-into-Greek interpretation, 17 subjects chose correctly term 1 (68%), 17 subjects chose correctly term 2 (68%), and 20 subjects chose correctly term 3 (80%). For the joint interpreting 22 subjects chose correctly term 4 (88%), 20 subjects chose correctly term 5 (80%) and 18 subjects chose correctly term 6 (72%). For the new interpretation, 18 subjects chose correctly term 7 (72%), 21 subjects chose correctly term 8 (84%) and 20 subjects chose correctly term 9 (80%). Finally, in the false interpretation, 22 subjects chose correctly term 10 (88%) and 20 subjects chose correctly term 11 (80%). We should note at this point that in two questionnaires (9 and 14) that did not have any selection of the term in the reference text, we deemed it as a wrong answer.

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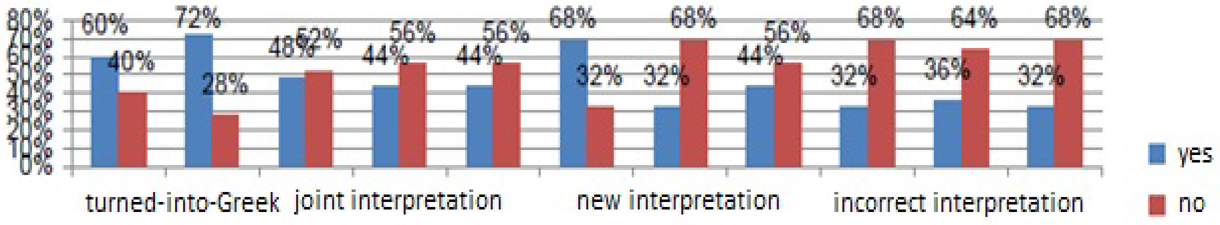
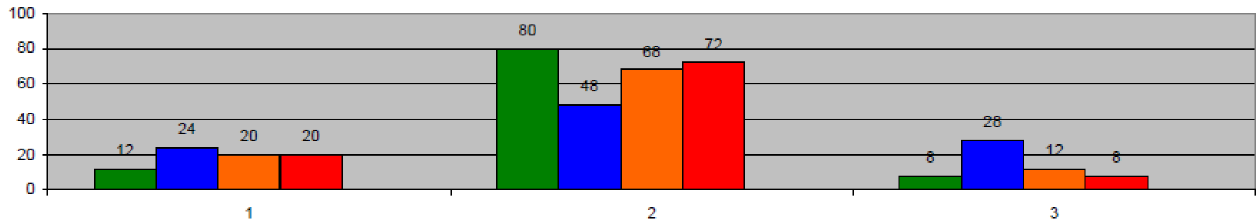


Figure 1: Term recognition-identification-usage



Memo: 1 blank 2 correct 3 wrong

Figure 2: Locating phrase correctness

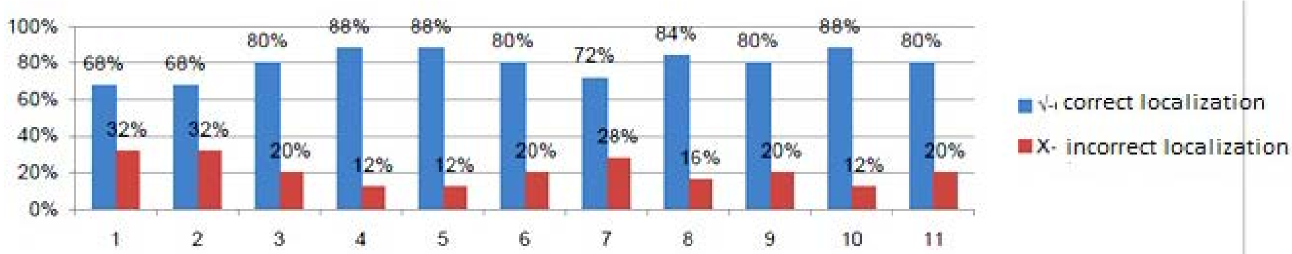


Figure 3: Correct term localization

4. RESEARCH CONCLUSIONS

The main impression that one gets out of the study of the questionnaires is that the effort for using Greek terminology was warmly welcomed. This means that the subjects show a positive attitude towards using purely Greek academic texts. This conclusion is drawn by: a) the fact that the purely proposed Greek terms were significantly recognized as already known, b) the relatively good pairing with the terms in the reference text, c) the acceptance of the incorrect interpretation as correct, despite the fact that its terms were recognized as known in advance. The latter raised great puzzlement and was the reason for the index processing of the academic texts of Telecommunications.

Initially, the frequent occurrence of a free translation should be noted where several strategies were used, always in text proposal cases, as those of the following terms: "Coding for deep-space communication", "Duo-binary signaling, error probability", "MLSD, path memory truncation".

In general, after the processing of the indexes, an unprecedented phenomenon for scientific work was ascertained, that of the English lemmas introduction for indexing, either as complete individual words or acronyms, or as the first parts of complex terms. The habit, or rather the norm, is that the lemmas are indexed separately by languages. Conversely, in this particular case we examined, there is a mixture, even without clear categorization criteria, since it occurs sometimes graphemic, either before or after the Greek lemmas, and sometimes phonemic. This hampers the reader greatly, who is the student of the Department of Telecommunications. For the Greek

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literature, such indexing is not acceptable, as this is an obvious example of the already established domination of English on the Greek.

5. GENERAL CONCLUSIONS

The mere existence of several scientific errors prevents us to talk about the complete accuracy of the content and, of course, leads us to observe the ambiguity of terminology. Moreover, due to the detection of incorrect syntactic structures, we doubt whether the compatibility between common language and terminology has been achieved. Of course, in a communicative way the translation manages to remain equivalent to the original text, as it is required to achieve the same purpose and this is obvious in all its style. However, because the grammar-syntactic rules of the Greek language were not followed to a significant degree, we cannot clearly say that this translation is typical of the Greek scientific literature.

6. PROPOSAL FOR THE ENVIRONMENTAL SCIENCE FIELD

We believe that by using the aforementioned bilingual control mechanism in the environmental science field, it would assist for building consensus and hence a standardized Greek terminology in the environmental domain which constitutes a top priority. In particular, at university level, this should constitute a primary concern. Those who will promote science in the future are being prepared by the academic community and it is necessary to teach them the use of national terminology, but above all the right use of the Greek language.

We also consider that a result of this suggestion, would not only be the promotion of Greek language and terminology at national level but also the reassurance of a better and more effective communication between scientists, as well as the improvement of the provided teaching to students who will be able to study, through translation, the foreign-language bibliography without encountering ambiguities and problematic terms with double or even triple translation versions.

We hope that this paper will contribute towards this direction and that the resulting data after further research will lead to better training of scientists and official translators as well as contribute to more efficient and qualitative science handbooks, bilingual glossaries, and terminology databases.

References

[1] Ladmiral, J. 1979. *Traduire: théorèmes pour la traduction* (Translating: Theorems for translation). Payot, Paris.
[2] Toury, G. 1995. *Descriptive translation studies and beyond*. John Benjamins, Amsterdam/Philadelphia.
[3] Newmark, P. 1995. *Approaches to translation*. Phoenix ELT, New York.
[4] Newmark, P. 2005. *A textbook of translation.* Longman, Essex, England.
[5] Reiss, K. 1983. *Texttyp und Ubersetzungsmethode: D. operative Text*. Julius Groos Verlag, Kronberg/Heidelberg.
[6] Nord, C. 1997. *Translating as a purposeful activity: Functionalist approaches explained*. St. Jérôme, Manchester, United Kingdom
[7] Koller, W. 1992/1978. *Einführung in die Übersetzungswissenschaft* (Introduction to the translation science). Quelle & Meyer, Heidelberg, Wiesbaden.
[8] Hatim, B., Mason, I. 1997. *The translator as communicator*, Routledge, London
[9] Delabastita, D. 1989. Translation and mass communication: Film and T.V. translation as evidence of cultural dynamics. *Babel*, **35(4)**, 193-218.
[10] Hann, M. 1992. *Technical translation Vl. 2 terminology/lexicography.* John Benjamins, Amsterdam/Philadelphia.
[11] Lerat, P. 1995. *Les langues spécialisées* (Languages for special purposes). Presses universitaires de France, Paris.
[12] Lausberg H. 1960. Handbuch Der Literarischen Rhetorik, Max Hueber, München.
[13] Christidou, S. 2007. *Μεταφραστικές Δυσκολίες Ακαδημαϊκών Κειμένων Τηλεπικοινωνιών (Αγγλική <> Ελληνική). Αξιολόγηση Μεταφραστικών Συμπεριφορών* (Translation difficulties of telecommunications academic texts (English <> Greek). Evaluation of Translators' Behaviors). Retrieved from http://invenio.lib.auth.gr/record/100715/files/gri-2008-1031.pdf (accessed April 10th 2016).

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[14] Christidou, S. 2014. *Στρατηγικές Μετάφρασης με εφαρμογή στα Ειδικά Πεδία της Γλώσσας και των Τηλεπικοινωνιών* (Translation strategies with application in the special fields of linguistics and telecommunications). Florina, Thessaloniki: Iliadis Publications. (Three-member committee: Supervisor Kamaroudis E. Stavros: Associate Professor of The University of Western Macedonia, Chrysoulidis P. Dimitrios: Professor, School of Engineering, Department of Electrical and Computer Engineering, Fahantidis Nikolaos: Associate Professor, University Of Western Macedonia, Department of Informatics and Telecommunications Engineering.) Retrieved from http://www.didaktorika.gr/eadd/ (accessed April 14th 2016).
[15] Tchobanoglous, G., Kreith, F. 2002. *Handbook to solid waste management*. 2nd ed. Mc Graw-Hill, New York, USA.
[16] Tchobanoglous, G., Kreith, F. Μετάφραση: Κούγκολος, Α., Καραγιαννίδης, Α., Σαμαράς, Π. 2010. *Εγχειρίδιο διαχείρισης στερεών αποβλήτων*. 2η έκδ. Εκδόσεις Τζιόλα, Θεσσαλονίκη.

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Waste Minimization and Pollution Prevention

PROTECTION
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XIII

Treatment of solid copper wastes with ammonia-based reagents to yield saleable copper

F. J. Alguacil*, I. Garcia-Diaz, F. A. Lopez, O. Rodriguez

Centro Nacional de Investigaciones Metalurgicas (CSIC), Avda. Gregorio del Amo 8,
28040 Madrid, Spain.
*Corresponding author: Email: fjalgua@cenim.csic.es

Abstract

Copper flue dusts from three types of copper smelting furnaces were leached with different ammonia-based reagents (ammonium chloride, ammonium carbonate and aqueous ammonia solutions) to dissolve the oxidised copper species via the formation of copper-ammonia complexes, so that most of the copper-accompanying metals especially iron, remained in the solid residue. The as obtained copper pregnant solutions were treated via liquid-liquid extraction or cementation operations. In the first case, oxime derivatives or β-diketones dissolved in a kerosene type diluent were used as organic extractants in a continuous circuit, whereas in the case of cementation, zero valent zinc was used as cementing agent for copper. The end and saleable products from the above processes are grade A copper cathode or copper cement, respectively. As a concluding remark, these ammonium-based leaching media seemed suitable for the recovery of the oxidised Cu species from the dusts.

Keywords: copper solid wastes; leaching; solvent extraction; Cementation

1. INTRODUCTION

Taking into account the actual copper prices in the market (around 4400 Euro/t as time of writing March 2016), the recovery of this metal from a given raw material and even secondary sources is of a profitable interest. Among copper-bearing second sources, copper flue dusts are of interest due to their relatively medium-high copper content and because they are considered as hazardous materials and can not be dumped as such. Moreover, their recycling to the correspondent furnace it is not always desirable for different reasons.

Accordingly with the European Copper Institute [1], a copper flue dust is defined as the product recovered from exhaust gas streams found in furnaces, flues and settling chambers as a result of roasting, smelting and converting operations from copper refining processes. The elements presented in the final product can vary accordingly with the material used in a given furnace. The consideration of such dusts as hazardous materials is due to their toxicological and harmful properties causing various diseases (Table 1).

Table 1. Some harmful properties and effects of copper flue dusts.

Hazard class and code	Effect
Acute toxicity 3 (inhalation)	Toxic if inhaled (H331)
Skin sensivity 1	Probable allergic skin reaction (H317)
Carcinogenic 1A	Probable cancer (H350)
Repetitive exposure 1 (inhalation or ingestion)	Damage to organs: central nervous system, blood, kidney (H372)

This work presented an investigation about the treatment of different copper flue dusts by the use of ammonia-based leachants (it is known the closed ability between copper(II) and ammonia to form soluble and stable complexes in aqueous solutions) and the recovery of copper from the copper-bearing solutions via liquid-liquid extraction or cementation operations, resulting both in a final saleable copper material, copper cathode or copper cement, respectively.

2. MATERIALS AND METHODS

The three copper flue dusts, considered in this work, are of Chilean nature and they come from flash, reverberatory and converter furnaces. Their copper content are shown in Table 2.

Table 2. Copper content of the flue dusts.

Type	%Copper	Mineralogical species
Flash	25	copper sulphates and oxides, iron oxides, sulphides
Reverberatory	27	copper oxides and sulphates, sulphides, copper/iron oxides
Converter	74 (30% metallic copper)	metallic copper, copper/molybdenum/iron sulphides,arsenic-copper species

Other elements (iron, arsenic, molybdenum, etc.) regularly appeared in the starting material. A x-ray diffraction sight showed that the mineralogical species found in this secondary materials are also of a various nature (Table 2). The physical aspect of the dusts is of typical powders, except in the case of the converter dust which is formed of spherical or near-spherical balls (Figure 1).

All the reagents used in the present work were of AR grade, except the extractants LIX 860 (aldoxime), LIX 84 (ketoxime) and LIX 54 (β-diketone) which were supplied by Cognis Ltd. (Ireland). They were used as such by diluting them to the desired concentration with Exxsol D100 diluent, supplied by Exxon Chem. Iberia (Spain), which is a kerosene type diluent with >97% aliphatic components.

Leaching experiments were conducted under mild conditions, that are at room temperature and under atmospheric pressure, in a glass reactor, in order to decrease the operational costs, though these expenses were not evaluated within the frame of this investigation. Experiments were run up to three hours time, however different runs showed that two hours are often the limiting time to ensure a maximum copper recovery from the dusts.

Based in previous batch experiments [3-5], continuous liquid-liquid extraction experiments were conducted in a unit of mixer-settlers. The unit has a maximum flow capacity of 100 ml/min for each phase (aqueous feed, organic and aqueous stripping), whereas mixing and settling volumes were 200 and 700 mL, respectively. The solutions in the mixers were mixed by impellers.

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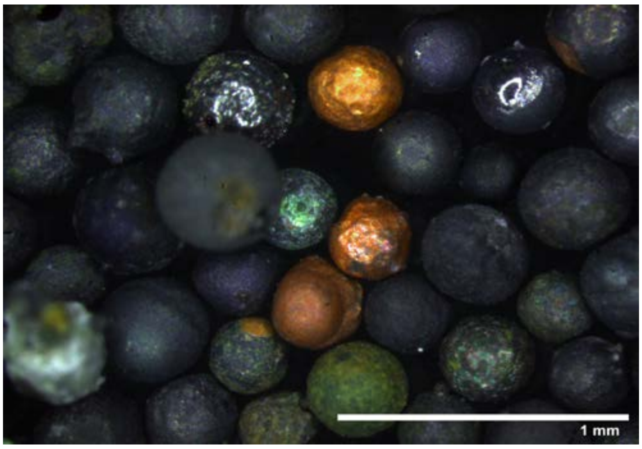


Figure 1.
View of the converter dust (the orange forms are of zero valent or metallic copper). Source photo: D.Martinez and F.J.Alguacil, 2016.

Cementation experiments were carried out in a glass reactor provided with a gently mechanical shake (200 min^{-1}) in order to maintain the solution under agitation. At this solution, the cementation agent was added.

Metals in solution were analysed by AAS.

3. RESULTS AND DISCUSSION

3.1 Leaching

This investigation uses various concentrations of ammonia-based reagents as the leaching medium, these leachants have some singularities derived from the weak acid nature of the ammonium ions:

$$NH_4^+ \Leftrightarrow NH_3 + H^+ \quad (1)$$

thus, the leachants produced ammonia, which forms highly stable complexes with copper(II), increasing the solubilization of the species contained in the starting material, i.e.:

$$CuO + 4NH_3 + H_2O \rightarrow Cu(NH_3)_4^{2+} + 2OH^- \quad (2)$$

however, and with any of the leachants investigated in this work, with the continuous generation of ammonia in the aqueous solution, the pH values of such solutions do not change significantly due to the fact that copper(II) form highly stable ammonia complexes, resulting in that the ammonia formed during leaching becomes bonded in the form of copper-ammine complexes, and only an amount of non-bonded ammonia in equilibrium remained as free ammonia in a relative concentration of the corresponding leachant. This constitute a kind of buffer system which keeps the pH value for each solution almost constant. Besides the copper dissolution, the most important consequence of the above is the high purity of the solution obtained, and particularly is iron free because due to the high pH values of the solutions, all the iron contained in the copper dusts remains in the solid residue basically as iron(III) oxide [2].

The results of the leaching experiments are summarized in Tables 3-5. It can be seen that with the flash dusts the maximum in copper recovery is regularly obtained, whereas the minimum is obtained in the case of the converter dust, very probable due to the considerable presence of zero valent or metallic copper in the starting material, which remained unattacked under the mild conditions used in the present work, and practically the same occurred with the sulphides species of the dusts. Practically in all the cases, the percentage of copper recovered increases with the decrease of the pulp density, whereas in the case of aqueous ammonia leachant, the increase of the leachant concentration does not affect very appreciably to the percentage of the copper recovered from the dusts.

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Table 3. Leaching with ammonium chloride solutions of copper dusts.

Run	Type of dust	Leachant	Pulp density %wt	% Cu leached
1	flash	1 M	4.8	90
2			0.99	90
3	reverberatory	1 M	4.8	14
4			0.99	28
5	converter	1 M	4.8	3
6			0.99	23

pH of the solutions 5.5±0.3

Table 4. Leaching with ammonium carbonate solutions of copper dusts.

Run	Type of dust	Leachant	Pulp density %wt	% Cu leached
7	flash	1 M	4.8	45
8			0.99	81
9	reverberatory	1 M	4.8	29
10			0.99	34
11	converter	1 M	4.8	7
12			0.99	19

pH of the solutions 8.5±0.1

Table 5. Leaching with aqueous ammonia solutions of copper dusts.

Run	Type of dust	Leachant	Pulp density %wt	% Cu leached
13	flash	15 M	0.99	81
14		1 M	0.99	75
15	reverberatory	15 M	0.99	34
16		1 M	0.99	31
17	converter	15 M	0.99	20
18		1 M	0.99	7

pH of the solutions 11±0.5

3.2 Liquid-liquid extraction

The liquid-liquid extraction (LLE) operation transfers dissolved copper(II) from the low-copper and/ or impure pregnant leach solution to high-copper pure electrowinning electrolyte solution, being this operation critical to ensure a correct copper solution to enter into the electrowinning operation.

Basically, the LLE operation consists of four steps:

i) transfer the copper from the leach solution into an organic phase,
ii) separation by gravity of the two phases or solutions,
iii) transfer the copper from the loaded organic phase to an acidic solution (spent electrolyte), and
iv) separation by gravity of the two phases or solutions and recycle of the organic phase to a new extraction step.

Transfer of copper into the organic phase is favoured by the low acidity or nil of the pregnant leach solution:

$$Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow CuR_{2_{org}} + 2H^{+}_{aq} \qquad (3)$$

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whereas copper transfer from the organic phase to the spent electrolyte solution is favoured by the high acid concentration of the electrolyte:

$$CuR_{2_{org}} + 2H^{+}_{aq} \Leftrightarrow Cu^{2+}_{aq} + 2HR_{org} \quad (4)$$

In practice, the figures for LLE operation are summarized as in Table

Table 6. Generalities for copper LLE operation.

Stage	Cu in aqueous	Acidity	%v/v extractant
Extraction	1-5 gL^{-1}	low	5-20
Stripping	30-50 gL^{-1}	high	5-20

Very often, the acidity of the aqueous solution in the extraction stage is in the order of pH 2 and higher, whereas in the stripping step the spent electrolyte contained 150-180 gL^{-1} sulphuric acid and 25-35 gL^{-1} copper(II), the advance electrolyte or the aqueous stripping solution exiting the LLE operation and entering the electrowinning operation contained near 30-50 gL^{-1} copper(II) and 150-170 gL^{-1} sulphuric acid. As organic extractants, the operation uses ketoximes, aldoximes, tailored mixtures of both and β-diketones, the latter commonly used when the pregnant solution is ammoniacal (pH>10) medium [4]. These reagents are usually dissolved in kerosene type diluents to reach the desired extractant concentration necessary for each LLE operation.

In the present investigation, LIX 860, LIX 84 and LIX 54 extractants were used to extract copper from three representative leach solutions generating in the treatment of copper dusts with ammonium chloride (pH 5.5), ammonium carbonate (pH 8.5) and aqueous ammonia solution (pH 11), in all the three cases, a solution of 180 gL^{-1} sulphuric acid was used as strippant for the respective copper-loaded organic solutions.

In the present case, the copper extraction reaction represented by eq. (3) is substituted by:

$$Cu(NH_3)^{2+}_{4_{aq}} + 2HR_{org} \Leftrightarrow CuR_{2_{org}} + 2NH^{2+}_{4_{aq}} + 2NH_{3_{aq}} \quad (5)$$

in which the protons resulting by the extraction of copper(II) and released to the aqueous solution are neutralized by the ammonia from the copper(II)-ammonia complex. The stripping reaction represented by eq. (4) is maintained, and in this case served to back the copper to an acidic solution suitable for electrowon. In all the above eqs (3-5), the subscript aq denotes the aqueous solution, whereas the subscript org denotes the organic phase.

Table summarized the operational conditions for the three systems:

Table 7. Operational conditions for the counter-current extraction of copper.

Reagent[a]	Extraction+stripping stages	Vo/Va ratio in extraction	Vo/Va ratio in stripping	Neat Cu gain, gL^{-1}
LIX 860	1+2	1/1	2/1	1.9
LIX 84	2+2	1/2	2/1	7.7
LIX 54	1+2	1/2	2/1	5.7

[a] at 20% v/v in Exxsol D100. Vo: volume of organic phase. Va: volume of aqueous solution.

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Figures 2, 3 and 4 showed schematic flow sheets for each one of theses operation, which were run for 20 hours each. Overall yields in terms of copper transfer exceeding 98% in all the three cases.

3.3. Cementation

Cementation is an hydrometallurgical operation in which a metal, in its ionic form, is precipitated from the aqueous solution by another but zero valent metal. In this process, the metal with the more positive oxidation potential, as given in the electromotive series, goes to the solution and displaced or reduced a metal with a less positive potential. In practice, several cautions must be obeyed due to the probable side-reactions which take place during the operation, i.e. excessive dissolution of the cementing metal, redissolution of the precipitated metal, precipitation of hydrolytic products, etc.

Since in the present case, the copper-bearing solutions obtained from the leach operation have pH values above 2-3 (the pH range in which iron(III) precipitates), the use of zero valent iron is not recommendable since this new precipitate will contaminated the cemented copper, instead, a metal which remained solubilized in the ammoniacal medium should be used, and in the present investigation zero valent zinc was used as cementing agent for copper.

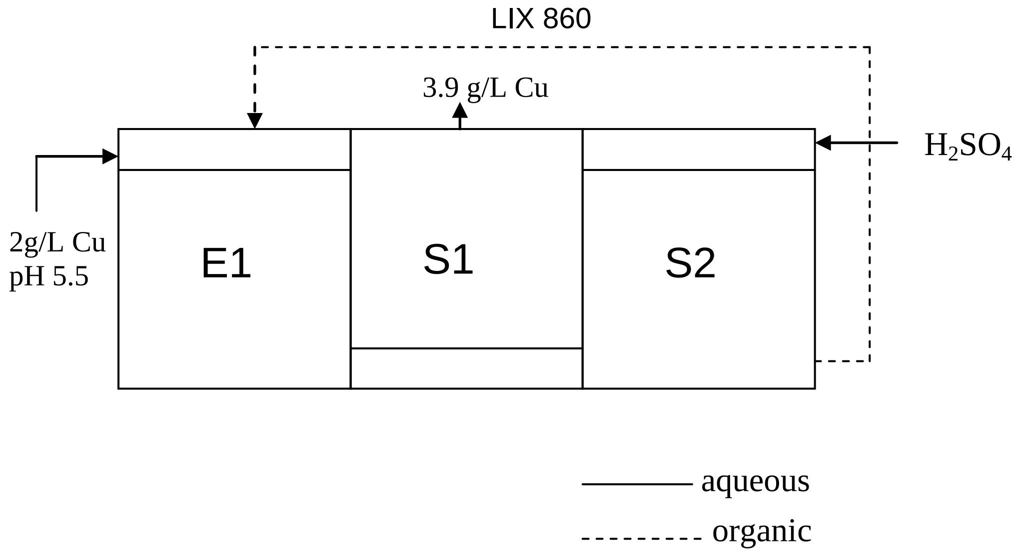


Figure 2. Schematic flow-sheet for the counter-current extraction-stripping circuit using LIX 860 as extractant for copper. Temperature: 20º C.

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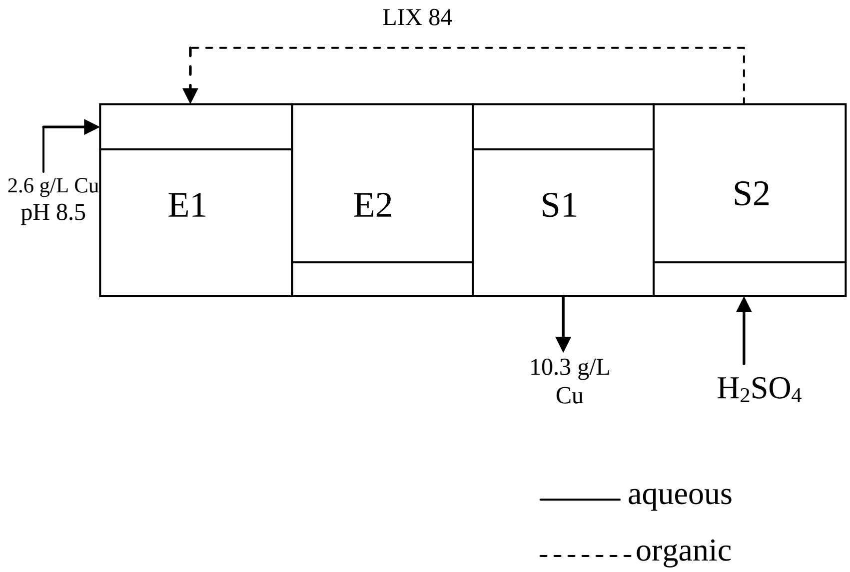


Figure 3. Schematic flow-sheet for the counter-current extraction-stripping circuit using LIX 84 as extractant for copper. Temperature: 20º C.

Accordingly with the electromotive series, the use of zero valent zinc

$$Zn/Zn^{2+} \quad E= +0.763 \text{ Volts}$$

can be used to cement copper

$$Cu/Cu^{2+} \quad E= -0.337 \text{ Volts}$$

and the dissolved zinc is stabilized in the aqueous solution via the formation of the zinc-ammonia complexes, i.e.

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \qquad (6)$$

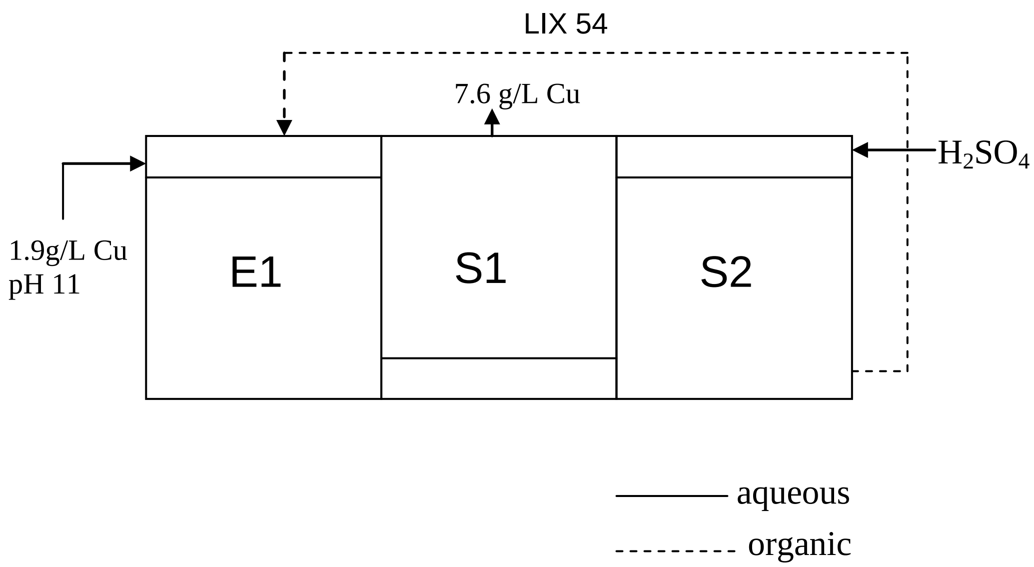


Figure 4. Schematic flow-sheet for the counter-current extraction-stripping circuit using LIX 54 as extractant for copper. Temperature: 20º C.

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In the case of solutions in ammonium carbonate medium, the increase in the Zn/Cu molar relationship, increased the cementation kinetics, though after two hours the extent of copper cementation is greater than 95% (Table 8)

Table 8. Influence of the Zn/Cu molar relationship on the percentage of copper(II) cementation.

Zn/Cu	15 min	30 min	60 min	2h
8	84	95	>99	>99
6	53	64	81	98
4	49	61	73	98

Aqueous solutions: 5 gL^{-1} copper and 0.6 M ammonium carbonate, pH 8.5. Temperature: 20º C

When the aqueous solution contained different concentrations of ammonium carbonate, it was found that the presence of this salt in the starting solution influences the copper cementation, increasingly this cementation as the salt concentration is increased (Table 9), however, at the lowest ammonium carbonate concentrations the cementation of copper by zinc is feasible if an excess of the cementation agent is used, as results in Table 8 shown.

Table 9. Influence of the ammonium carbonate concentration on the percentage of copper(II) cementation

Ammonium carbonate, M	15 min	30 min	60 min
0.6	13	13	14
0.8	35	46	45
1	65	87	97
2.4	69	88	>99

Aqueous solution: 10 gL^{-1} copper in ammonium carbonate, pH 8.5. Zn/Cu molar ratio: 2. Temperature: 20º C

The presence of aqueous ammonia in the solution decreased the percentage of copper cemented by zinc, as results in Table 10 shown. Probably this can be attributable to the presence of an excess of the complexing agent in the most ammoniacal concentrated solution, which besides the pH of the solution also probably change the copper(II)-ammonia complexes stoichiometries $Cu(NH_3)_n^{2+}$ (n= 1 to 4).

Table 10. Influence of the aqueous ammonia concentration on the percentage of copper cementation.

Aqueous ammonia concentration, M	% Copper cemented[a]
15	75
1.8	82
0.88	93

Aqueous solution: 2 gL^{-1} Cu in aqueous ammonia, pH 8.9-11. Zn/Cu molar ratio 2. Temperature: 20º C .[a]After 1 hour.

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The final material obtained in the cementation from a 0.88 M aqueous ammonia medium, presented a composition of 55% copper, 35% zinc and probably 10% balance oxygen, whereas the molar ratio of zinc dissolved against the copper cemented is near 1, as expected by the reaction:

$$Cu^{2+} + Zn^{0} \rightarrow Cu^{0} + Zn^{2+} \tag{7}$$

This is not the case of the cementation from concentrated ammonia solutions in which the molar ratio of zinc dissolved against the copper cemented is near 2, indicating that side reactions occurs like an excessive dissolution of the cementing agent, probably due to the medium in which cementation takes place.

Conclusions

The use of ammonia-based leachants, and in mild conditions, in the recovery of copper from copper flue dust is attractive when the starting materials have a minimum of non-soluble species such as sulphides and metallic copper. In any case, copper solutions of a great purity are regularly obtained, and from this the final recovery of saleable copper products via liquid-liquid extraction or cementation is of interest. Three liquid-liquid extraction circuits have been proved in this investigation, resulting in solutions which can enter to a copper electrowinning plant. Cementation with zinc is also attractive, though the purity of the final product tends to be less than above.

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References

[1] http://www.copperalliance.eu (accessed March, 2016).
[2] Limpo, J.L., Luis, A., Hernandez, A., Alguacil, F.J., 1985. Spanish Patent 545698.
[3] Alguacil, F.J., 1999. Recovery of copper from ammoniacal/ammonium carbonate medium by LIX 973N. *Hydrometallurgy*, **52,** 55-61.
[4] Bermejo, J.C., Alonso, M., Sastre, A.M., Alguacil, F.J., 2000. Solvent extraction of Cu(II) by LIX 54-100 and its application to a solid supported liquid membrane system. *J. Chem. Res. (S)*, **9,** 479-481.
[5] Alguacil, F.J., Cobo, A., Alonso, M., 2002. Copper separation from nitrate/nitric acid media using Acorga M5640 extractant. Part I: solvent extraction study. *Chem. Eng. J.*, **85,** 259-263.

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Investigation of a common textile surfactant: biodegradability, toxicity, and photochemical treatment

C. Turker, T. O. Hanci, M. O. Cabuk, F. G. Babuna*

Department of Environmental Engineering, Istanbul Technical University, 34469, Istanbul, Turkey
*Corresponding author: Email: germirliba@itu.edu.tr

Abstract

The main objective of this study is to appraise the biodegradability, toxicity and photochemical treatability of a segregated textile effluent bearing a non-ionic surfactant. The segregated stream has a COD of 520 mg/L and a TOC of 240 mg/L that is completely soluble. The distribution of COD at different molecular weight cut-offs for raw wastewater shows that approximately 90% of the COD originates from a molecular weight cut-off range less than 30 kDa fraction. The aerobic biological treatment outlet contains a residual COD level of approximately 9% of the inlet COD. 120 minutes UV-C treatment of the segregated textile bath discharge at pH 4.0 results in a TOC removal of 45%. Increasing the initial reaction pH, however, is observed to reduce both the rate and extent of TOC removal. According to the empirical relationship found for UV-C application, approximately 8 and 15 mg H_2O_2 are used to mineralize 1 mg TOC at pH 4.0 and 11.0, respectively. Acute toxicity tests employing *V. fischeri* show increased toxicity with the application of 60 and 90 minutes photochemical treatment.

Keywords: *inert COD; photochemical treatment; surfactant; textile bath discharge; toxicity*

1. INTRODUCTION

Manufacturing processes generate segregated wastewater streams that might hold different toxicity and biodegradability levels. Such an output is an expected one as various auxiliary chemicals with different toxicity and biodegradability characteristics are fed during different stages of industrial operations. In this respect research activities on alternative textile auxiliaries that lower either energy requirements or water input or wastewater pollutant loads [1], together with specific treatment options applicable to segregated textile effluent streams are intensified [2-6].

Surfactants are among the commonly applied auxiliaries in textile wet mills from which chemical laden effluents arise. In some cases, the surfactants contribute more than 30% of the organic pollution in wastewaters originating from textile finishing plants [7]. Besides various surfactants are fed into textile wet mill operations, among which more than 500 are non-ionic in nature [8]. Biodegradability of non-ionic surfactants depends on the size of the molecule and the degree of branching [9]. Some surfactants exert high recalcitrance due to the presence of aromatic rings in alkyl chain [9]. Studies are performed to search ecotoxicological properties of commercial surfactants [3-6, 10-12].

Biological treatment is the most commonly applied method to textile effluents as it yields the most cost effective solution [13]. However, some segregated textile wastewaters where auxiliary chemicals are added might cause problems related to their high recalcitrance and toxicity in biological treatment. Therefore, it is recommended to pass these problematic segregated bath discharges through a specific treatment previous to mix them with the rest of the effluents [14]. As stated in literature the economic and technical feasibility of applying solely AOP's to industrial wastewaters is questionable [15]. Yet partial oxidation by the use of AOP's to inert and/or toxic segregated industrial effluents may result in more biodegradable and/or less toxic outputs that can ease the subsequent biological treatment. Photochemical treatment by H_2O_2/UV-C oxidation is among the most effective treatment alternatives applicable to surfactant bearing textile effluents [7].

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In this context the purpose of this study is to assess the biodegradability, toxicity and photochemical treatability of a non-ionic surfactant carrying segregated textile wastewater stream. The COD distribution at various molecular size cut-off levels are presented. The results obtained on the application of H_2O_2/UV-C oxidation are evaluated. The effect of photochemical treatment on the acute toxicity towards *Vibrio fischeri* is investigated.

2. MATERIALS AND METHODS

The surfactant under investigation was obtained from a local textile dyeing and finishing mill in Istanbul, Turkey and used as received. It must be noted that the surfactant formulation contained H_2O_2. This surfactant was added in batch-wise preparation operations during viscose fabric production. After the application of the mentioned surfactant, viscose fabric was directed to dyeing step. Therefore, the major concern was the last stage of preparation. Figure 1 depicts the general production route together with the details of the textile bath where the surfactant was added. As given in Figure 1, in the last stage of preparation phase, 8 g/L of surfactant and 0.5 g/L of leveling agent were added to a textile bath where 100 kg of viscose fabric was processed at 60°C at a pH of 10 for about 45 minutes. Approximately 100% of the surfactant and the leveling agent remained unfixed onto the viscose textile material yielding a segregated wastewater containing all of the added surfactant and the leveling agent. Due to this fact to mimic the actual textile bath discharge where this textile surfactant was added, a sample was prepared by dissolving 4 grams of surfactant and 0.5 grams of leveling agent in 1 liter of water. This sample was subjected to the experimental studies.

Physicochemical and ecotoxicological characteristics of the surfactant as obtained from material safety data sheet, are summarized in Table 1. As can be seen from the table, the surfactant has low acute oral toxicity towards rats. However aquatic toxicity is of concern as the effluents of this facility will be discharged to a nearby marine environment.

2.1 Analytical Procedures

H_2O_2 in the samples was determined titrimetrically by employing the molybdate-catalyzed iodometric method [16]. COD was determined by following the closed reflux titrimetric method [17]. In order prevent H_2O_2 interference on COD measurements, prior to COD analysis H_2O_2 present in the samples was destroyed with enzyme catalase derived from *Micrococcus lysodeikticus* (Fluka). TOC was measured by using a Shimadzu VCPN model carbon analyzer (combustion method) equipped with an auto sampler. All other analyses for conventional parameters were conducted according to Standard Methods [18]. The experiments were conducted at room temperature. pH was adjusted by introducing either NaOH or H_2SO_4 solutions. pH values were measured with an Orion720+ model pH-meter. Filtrates of samples subjected to vacuum filtration by means of Millipore membrane filters having a pore size of 0.45 μm were defined as soluble fractions. Each data point was calculated as the mean of three replicate measurements. Experiments were repeated until obtaining statistically indifferent results.

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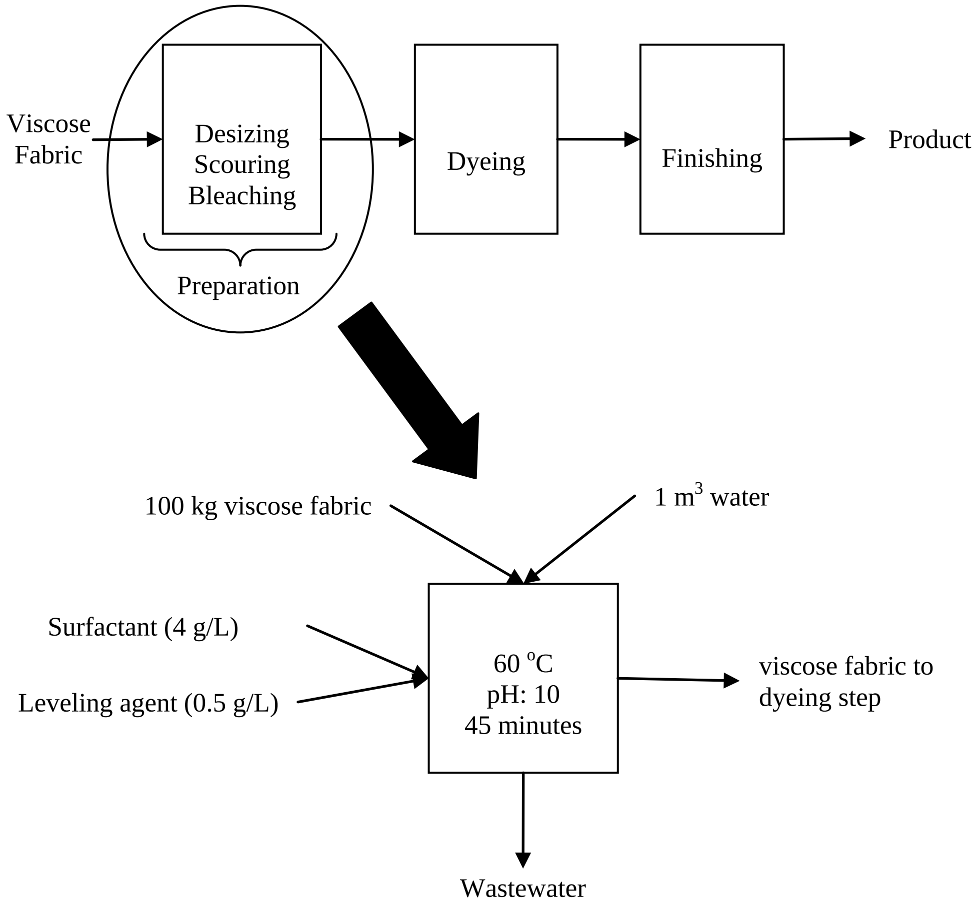


Figure 1. General production flowchart and the textile bath under investigation

Table 1. Characteristics of the surfactant as obtained from the product safety data sheet

Appearance	Cream coloured granules with a characteristic odour
Ingredients	Ethoxylated alcohol mixture (Non-ionic surfactant)
Density (g.cm-3)	1.1
pH	9.5 – 10.5 (1 gr/L)
Solubility	Highly water soluble
Acute oral toxicity (LD50*, mg.kg-1)	>2300

* Lethal dose causing 50 % death in rats;

2.2 Molecular size distribution

The COD distribution of the sample (textile bath discharge bearing the surfactant) at different molecular size cut-off levels was assessed. For this purpose, a series of filtration/ultrafiltration experiments were performed by using 400 mL-capacity cells (Amicon, Model 8400) under positive nitrogen gas pressure (0.4-2.5 bar) and continuous mixing. The segregated textile bath discharge

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was filtered through 1200-1600 nm (Millipore AP40), 450 nm (Durapore ® HV, PVDF) and 220 nm (Durapore ® GV, PVDF) cut-off filters under 0.7 atm pressure. Samples previously filtered through 220 nm membrane filters were subjected to ultrafiltration using 100, 30 and 10 kDa molecular size cut-off membranes under 3.7 atm pressure. Obtained permeates and retentates were analyzed for COD.

2.3 Inert COD

The experimental procedure given in literature for completely soluble wastewaters [19] was adopted for the assessment of inert COD content of the sample. According to the mentioned procedure two aerated cylindrical batch reactors with volumetric capacities of 3 liters, one fed with the textile bath discharge itself, and the other with glucose solution having the same dilution, were run. The seed was obtained from a lab-scale fill and draw aerobic reactor operated under steady state conditions for about 40 days with a food to microorganism ratio of 0.6 mg COD (mg VSS. day)$^{-1}$. A mixture of 50% glucose and 50% textile bath discharge sample was introduced as the feed for this fill and draw aerobic reactor used to generate the seed. An initial biomass concentration of 50 mg VSS L^{-1} was sustained in the batch reactors (both run with sample and with glucose) where inert COD tests were conducted. Such a low initial biomass is adopted to hinder the interference of the residual COD that can form from the endogenous respiration of initial inoculums. Aliquots removed periodically from the mixed liquor of each reactor (run with sample and with glucose) were analyzed for soluble COD. To avoid erroneous results, a strict accounting was kept for all samples removed from the bioreactors, so that any water loss by evaporation was replaced with tap water prior to sampling. When a stable soluble COD plateau was observed, the experiments were stopped. The threshold level indicating a stable soluble COD plateau was defined as getting less than 3-5 % variation between consecutive samples. During the operation of bioreactors, pH was maintained in the range of 7-8 (suitable for biological activity). Nitrification inhibitor (Formula 2533TM, Hach Company) was added to all bioreactors in order to prevent any possible interference induced.

2.4 Photochemical treatment

Photochemical treatment experiments were performed in a 3250 mL-capacity batch stainless steel photoreactor having a length 95 cm and a width of 6 cm. This photoreactor was equipped with a 40W low-pressure, mercury vapor sterilization lamp located at the center of the reactor in a quartz glass envelope. The incident light flux of the UV-C lamp at 253.7 nm and effective UV-C light path length were determined via H_2O_2 actinometry [20] as 1.44×10^{-5}einstein L^{-1} s^{-1} and 5.67 cm, respectively. The sample was continuously circulated through the UV-C photoreactor using a peristaltic pump at a rate of 400 mL/min, corresponding to a hydraulic retention time of 8 min in the photoreactor. In each experimental run, the surfactant bearing wastewater was fed to the photoreactor and a sample (at time t =0) was taken. At this point, the reaction was initiated by turning on the UV-C lamp. Samples taken for up to 120 minutes were analyzed for total organic carbon (TOC) and H_2O_2.

2.5 Acute toxicity

Acute toxicity tests were performed by using BioTox™ test kit (AboatoxOy, Finland) that is a commercial bioassay based on the inhibition of bioluminescence emitted by the *V. fischeri* marine photobacteria [21]. Accordingly, the lyophilized bacteria were rehydrated. 500 µL aliquots of the bacteria solution were pre-incubated for 15 min at 15°C. After measuring the initial bacteria luminescence, 500 µL of the diluted samples were added to the bacteria. The luminescence was again measured after the incubation time of 15 min at 15°C on an Aboatox C110 (AboatoxOy, Finland) BioTox apparatus. The IC_{20}, IC_{50} and IC_{80} values corresponding to the dilution ratio of samples that produces 20%, 50% and 80% effect on *V. fischeri*, respectively, of raw and treated

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segregated textile bath discharge were determined. Prior to acute toxicity tests the pH of all samples was adjusted to 7.0 ± 0.2.

3. RESULTS AND DISCUSSION

3.1 Conventional wastewater characterization and COD distribution at different molecular sizes

The segregated textile bath discharge where the surfactant under investigation is added, is completely soluble in nature. This effluent has a total COD of 520 mg/L, TOC of 240 mg/L, TKN of 23 mg/L, TP of 9.4 mg/L and a pH range of 9.5-10.5. The distribution of COD at various molecular weight cut-offs are presented in Figure 2. The results indicate that approximately 90 % of the COD originates from a molecular weight cut-off range less than 30 kDa fraction and 69 % of it is in <10 kDa range.

3.2 Inert COD

The organic content of industrial wastewaters is measured with COD. As total COD presents both biodegradable and inert organics, a fractionation is required to find out the inert portion that can be obtained after passing the effluent from biological treatment. The sum of the soluble residual (inert) microbial products, S_P, and the inert COD of influent origin, S_I, dictates the level of achievable COD at the outlet of a biological treatment plant [22]. The results of the inert COD experiment are tabulated in Table 3. The inert COD fractions presented in Table 4 are calculated by evaluating the figures obtained. Accordingly, out of 519 mg/L total COD, soluble inert COD accounts for 19 mg/L. Aerobic biological treatment effluent contains a residual COD level of 46 mg/L, corresponding to approximately 9% of the COD inlet. These findings indicate biodegradable nature of the segregated bath discharge.

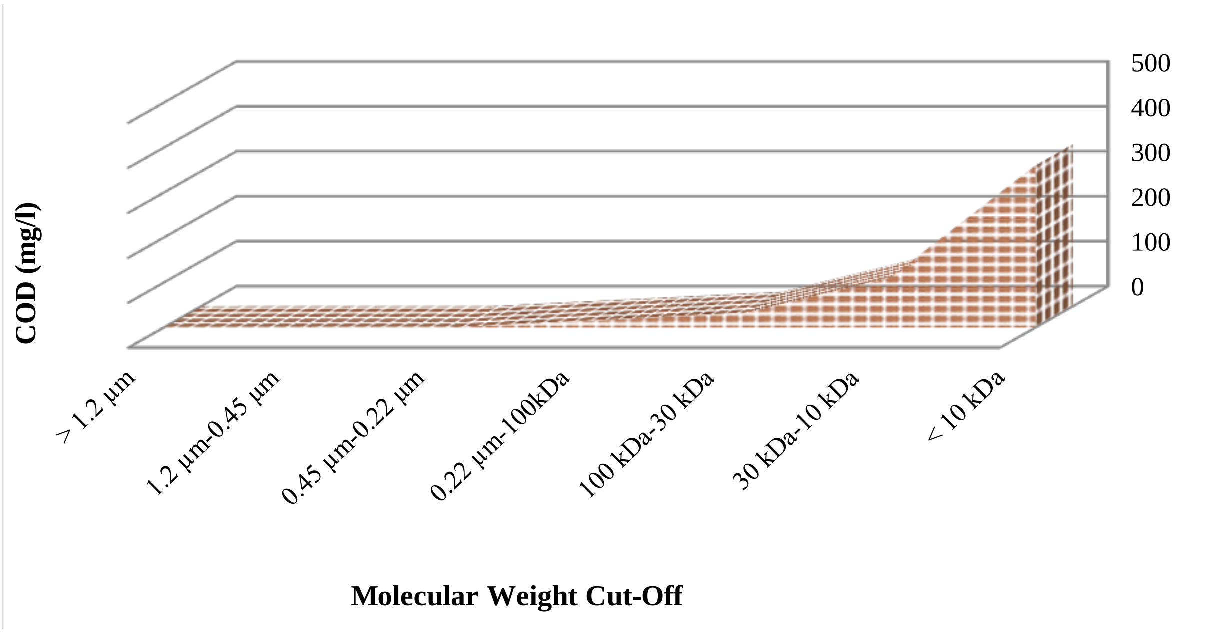


Figure 2. COD profile at different molecular sizes

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Table 3. Results of the inert COD experiment

	Soluble COD (mg/L) Reactor fed with	
	wastewater	glucose
Start of the experiment	519	518
End of the experiment	46	27
Duration (weeks)	13	13

Table 4. Inert COD fractions

Parameters	**(mg/L)**
COD of the Sample, C_T	519
Soluble Inert COD of the Sample, S_I	19
Soluble Microbial Products, S_P	27
Residual COD, $S_I + S_P$	46

3.3 Photochemical treatment

Figure 3 (a) and (b) shows TOC removal and H_2O_2 consumption rates during photochemical treatment of segregated textile bath discharge at pH 4.0 and 11.0, respectively. As can be seen from the figure, the average TOC value reached at the end of photochemical reaction period (120 minutes) is 137 mg/L at pH 4.0. This finding corresponds to an ultimate TOC removal efficiency of 45%. The oxidation of the organic carbon content continues during the course of photochemical treatment. 85% of the initially present H_2O_2 is utilized at the end of 120 minutes treatment period at pH 4.0. Taking into consideration that TOC removal and H_2O_2 consumption follow a similar trend, a linear relationship could be established for the obtained TOC removal and H_2O_2 consumption rates as presented in Figure 4. According to the empirical relationship found for these two process parameters, approximately 8 mg H_2O_2 is used to mineralize 1 mg TOC during the photochemical treatment of segregated textile bath discharge at pH 4.0.

It is evident from Figure 3 (b) that TOC removal is inhibited at pH 11.0 as at the end of 120 minutes 36% TOC removal is achieved. This fact can be mainly attributed to the high reaction pH, where H_2O_2 dissociates to its conjugate base HO_2^- (pK_a = 11.65) and is only partly available in the reaction medium for UV-C light absorption. As mentioned above, the presence of H_2O_2 is essential for TOC removal because hydroxyl radical ($HO^\bullet$) production entirely depends on H_2O_2 availability and concentration [23]. Considerably higher H_2O_2 consumption rates are observed at pH 11.0 than at pH 4.0. H_2O_2 is totally consumed after 60 minutes of photochemical treatment at pH 11.0. It should be mentioned here that despite the complete utilization of H_2O_2, TOC removal is increased from 23% (obtained for 60 minutes) to 36% (obtained for 120 minutes) as shown in Figure 3(b). It is thought that the oxidation process continued as a consequence of the UV-C photolysis of degradation intermediates formed during the photochemical treatment. A linear relationship is also observed between TOC removal and H_2O_2 consumption data for oxidation experiments conducted at pH 11.0 (Figure 4). Approximately 15 mg H_2O_2 is used to mineralize 1 mg TOC for the treatment of segregated textile bath discharge when the reaction pH is adjusted to 11.0.

3.4 Acute toxicity

Considering the substantially better performance of photochemical treatment at pH 4.0, it is decided to perform the acute toxicity tests only for this pH. Table 5 presents the *V. fischeri* toxicities (IC values) obtained during photochemical treatment of surfactant wastewaters. As can be seen from

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Table 5, the original IC_{80} value, being 3.9, is decreased to 2.7 and 2.5 after 60 and 90 minutes of photochemical treatment, respectively. As is reported in the literature investigating the HO•-based treatment of alkylphenol ethoxlate type nonionic surfactants, the step-wise loss of side chain ethoxylate units of alkylphenol ethoxlates results in more persistent and lipophilic metabolites and the toxicity generally increases with the hydrophobic character of the molecule [24-26]. In the present case, as the oxidation progresses, a general increase in the *V. fischeri* toxicities is observed due to the fact that degradation products formed during photochemical treatment are more toxic than the parent effluent.

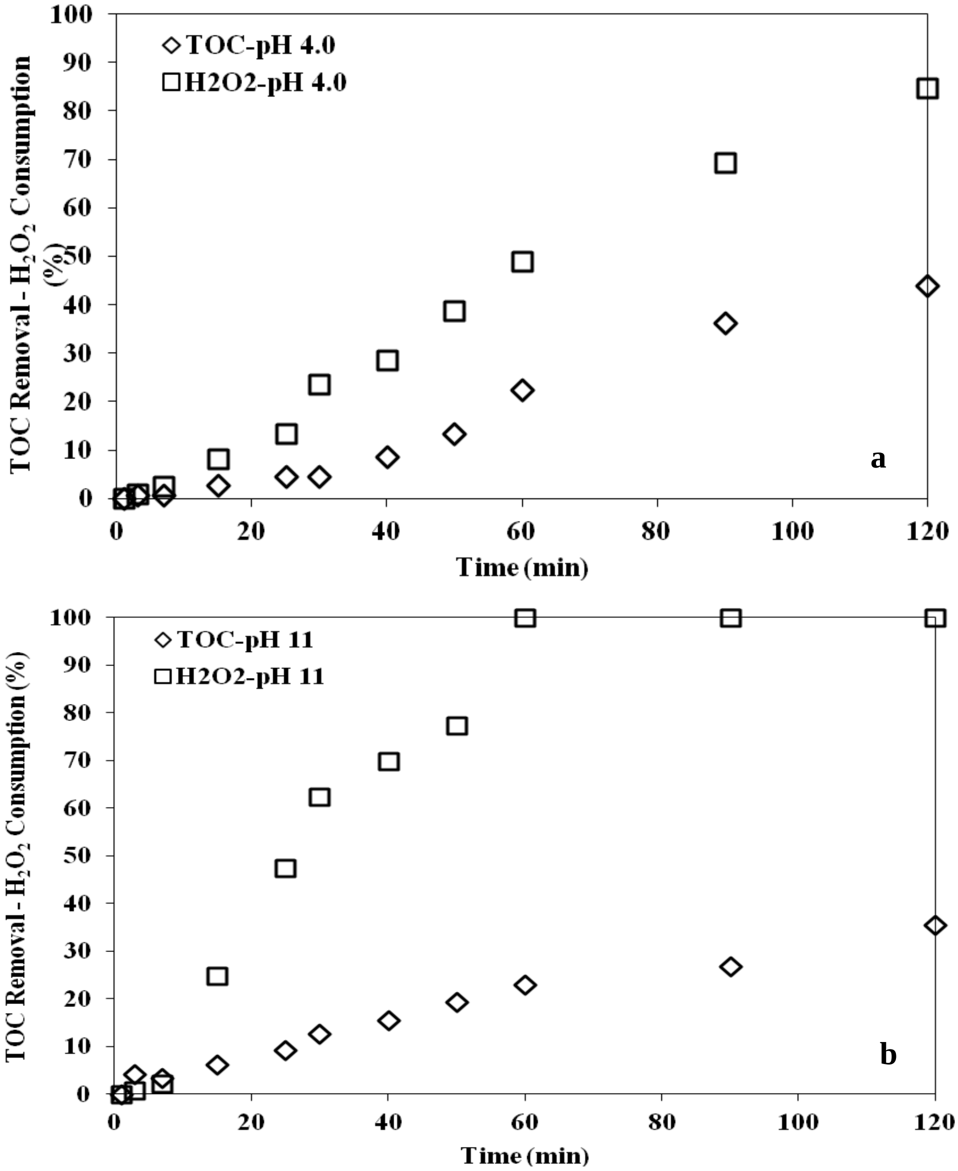


Figure 3. TOC removal and H_2O_2 consumption efficiencies obtained during the photochemical treatment of segregated textile bath discharge at pH 4.0 (a) and 11.0 (b)

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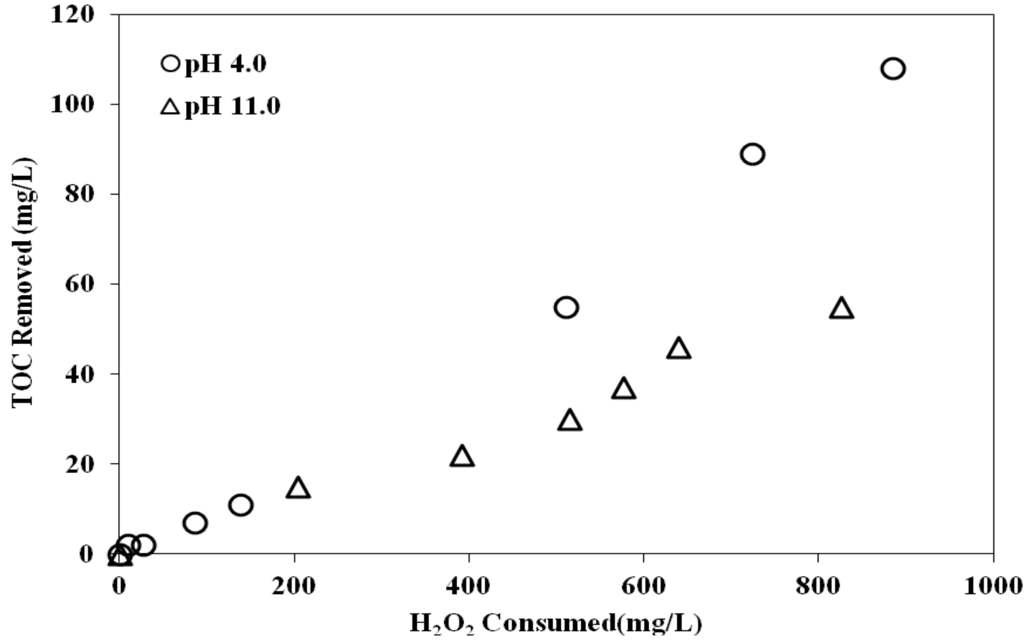


Figure 4. Relationship between TOC removal and H_2O_2 consumption obtained for the photochemical treatment of segregated textile bath discharge at pH 4.0 and 11.0

Table 5. Experimentally obtained IC values (%, v/v) for the raw (untreated) and for the photochemically treated (at pH 4.0) segregated textile bath discharge

		Photochemical Treatment Time	
	Raw surfactant wastewater	60 min	90 min
IC_{20}	0.7	0.4	0.5
IC_{50}	1.2	0.7	0.8
IC_{80}	3.9	2.7	2.5

4. CONCLUSIONS

The following conclusions are derived from this study performed on a segregated textile effluent bearing a non-ionic surfactant. The wastewater has a total COD of approximately 520 mg/L which is completely soluble. 90% of this COD originates from a molecular weight cut-off range less than 30 kDa fraction and 69% of it is in <10 kDa range. A residual COD level of 46 mg/L can be achieved by passing this segregated stream from aerobic biological treatment. This level corresponds to only 9% of the inlet COD indicating the biodegradable nature of the segregated stream. 120 minutes photochemical treatment of the segregated textile bath discharge at pH 4.0 results in 45% TOC removal. Increasing the pH from 4.0 to 11.0 decreases the TOC removal efficiency to 36%. Experiments conducted on *V. fischeri* reveal the formation of photochemical oxidation products with higher toxicities than the parent effluent. It is recommended to consider alternative treatment methods for this segregated textile stream due to the limited TOC removal efficiencies and elevated toxicity levels obtained with UV-C application.

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References

[1] Hasanbeigi, A. and Prince, L., 2015. A technical review of emerging technologies for energy and water efficiency and pollution reduction in the textile industry. *Journal of Cleaner Production*, **95**, 30-44.

[2] Arslan-Alaton, I. and Erdinc, E., 2006. Effect of photochemical treatment on the biocompatibility of a commercial nonionic surfactant used in the textile industry, *Water Research*, **40** (18), 3409-3418.

[3] Arslan Alaton, I., Iskender, G., Ozerkan, B., Germirli Babuna, F. and Okay, O., 2007. Effect of chemical treatment on the acute toxicity of two commercial textile dye carriers, *Water Science and Technology*, **55**(10), 253-260

[4] Germirli Babuna, F., Yilmaz, Z., Okay, O., Arslan Alaton, I. and Iskender, G., 2007. Ozonation of synthetic versus natural textile tannins: recalcitrance and toxicity towards Phaeodactylum tricornutum, *Water Science and Technology*, **55**(10), 45-52.

[5] Germirli Babuna, F., Camur, S., Arslan Alaton, I., Okay, O. and Iskender, G., 2009. The application of ozonation for the detoxification and biodegradability improvement of a textile auxiliary: Naphtalane sulphonic acid, *Desalination*, **249**, 682-686.

[6] Koyunluoglu, S., Arslan Alaton, I., Eremektar, G. and Germirli Babuna, F., 2006. Pre-ozonation of commercial textile tannins: Effects on biodegradability and toxicity, *Journal of Environmental Science and Health Part A*, **41**, 1873-1886.

[7] Arslan Alaton, I., Ubay Cokgor, E. and Koban, B., 2007. Integrated photochemical and biological treatment of a commercial textile surfactant: Process optimization, process kinetics and COD fractionation, *Journal of Hazardous Materials*, **146**, 453-458.

[8] Moore, S. and Ausley, L. W., 2004. Systems Thinking and Green Chemistry in the Textile Industry: Concepts, Technologies and Benefits, *Journal of Cleaner Production*, **12**, 585-601.

[9] Gonçalves, I. C., Lopes, L., Pinheiro, H. M., and Ferra, M. I. A., 2009. Behaviour of different anaerobic populations on the biodegradation of textile chemicals. *Journal of Hazardous Materials*, **172**, 1236-1243.

[10] Pavlic, Z., Vidakovic-Cifrek, Z. and Puntaric, D., 2005. Toxicity of surfactants to green microalgae *Pseudokirchneriella subcapitata* and *Scenedesmus subspicatus* and to marine diatoms *Phaeodactylum tricornitum* and *Skeletonema costatum*. *Chemosphere*, 61, 1061-1068.

[11] Tezgel, T., Germirli Babuna, F. and Iskender, G., 2014. An evaluation of commercial textile tannins based on their inert COD content and toxicity. *Global NEST Journal*, **16**(1), 52-58.

[12] Arslan-Alaton, I., Okay, O., Eremektar, G. and Germirli Babuna, F., 2006. Toxicity assessment of raw and ozonated textile biocides, *AATCC Review*, **6**(5), 43-48.

[13] Punzi, M., Nilsson, F., Anbalagan, A., Svensson, B. M., Jönsson, K., Mattiasson, B. and Jonstrup, M., 2015. Combined anaerobic-ozonation process for treatment of textile wastewater: Removal of acute toxicity and mutagenicity. *Journal of Hazardous Materials*, **292**, 52-60.

[14] Germirli Babuna, F., Turker, C., Oguz Cabuk, M. and Olmez Hanci, T., 2016. Biodegradability, toxicity and photochemical treatment of a textile surfactant. *Desalination and Water Treatment*, DOI: 10.1080/19443994.2016.1159995.

[15] He, Y., Wang, X., Xu, J., Yan, J., Ge, Q., Gu, X. and Jian, L., 2013. Application of integrated ozone biological aerated filters and membrane filtration in water reuse of textile effluents. *Bioresource Technology*, **133**, 150-157.

[16] OMA, 2005. *Official Methods of Analysis*, 18th ed., Association of Official Analytical Chemistry, Washington DC.

[17] ISO, ISO 6060, 1986. *Water Quality-Determination of the Chemical Oxygen Demand*, International Organization for Standardization, Geneva.

[18] APHA-AWWA-WPCF, 2003. *Standard Methods for the Examination of Water and Wastewater*, 21st ed., American Public Health Association, Washington DC.

[19] Germirli, F., Orhon, D., Artan, N., Ubay, E. and Görgün, E., 1993. Effect of two-stage treatment on the biological treatability of strong industrial wastewaters, *Water Science and Technology*, **28**(2), 145-152.

[20] Nicole, I., de Laat, J., Dore, M., Duguet, P. J. and Bonnel, C., 1990. Use of UV radiation in water treatment: Measurement of photonic flux by hydrogen peroxide actinometry. *Water Research*, **24**, 157-168.

[21] ISO, ISO 11348-3, 2007. *Water Quality - Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio fischeri (Luminescent Bacteria Test) - Part 3: Method Using Freeze-Dried Bacteria*, International Organization for Standardization, Geneva.

[22] Germirli Babuna, F. and Orhon, D., 2010. Biodegradation Characteristics of Wastewaters, Kay W. Canton, ed., in *Fluid Waste Disposal*, Nova Publishers, ISBN: 978-1-60741-915-0.

[23] Parsons, S., 2004. *Advanced oxidation processes for water and wastewater treatment*. IWA Publishing, London.

ISBN: 978-960-6865-94-7

[24] McLeese, D.W., Zitko, V., Sergeant, D.B., Burridge, L. and Metcalfe, C.D., 1981. Lethality and accumulation of alkylphenols in aquatic fauna. *Chemosphere*, **10**, 723-730.
[25] Hill, R.L. and Jans, D.M., 2003. Developmental estrogenic exposure in zebrafish (Danio rerio): I. Effects on sex ratio and breeding success. *Aquatic Toxicology*, **63**, 417-429.
[26] Karci, A., Arslan-Alaton, I., Olmez-hanci, T. and Bekbolet, M., 2013. Degradation and detoxification of industrially important phenol derivatives in water by direct UV-C photolysis and H_2O_2/UV-C process: A comparative study. *Chemical Engineering Journal*, **224**, 4-9.

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Hierarchical classification of supercapacitors; stroke degradation and their environmental issues in their End-of-Life phase

P. I. Kokkotis, C. S. Psomopoulos*, G. Ioannidis, S. Kaminaris

Department of Electrical Engineering, Piraeus University of Applied Sciences, 250, Thivon & P. Ralli Ave., 12244, Egaleo, Greece
*Corresponding author: Email: cpsomop@teipir.gr

Abstract

Supercapacitors (Ultracapacitors or Electric Double-Layer Capacitors) are high capacity electrochemical capacitors that can act as a bridge, in means of an electricity storage method, between common electrolytic capacitors and other means of electrochemical energy storage (i.e. batteries). A Supercapacitor consists of the electrodes, the electrolyte and the separator. This study reveals the various materials used in the manufacturing process of Supercapacitors, their pros and cons and classifies these materials, along with upcoming trends, regarding their potential environmental issues and the possible harm that can do to humans and the environment.

The wide varieties of materials (Ruthenium, Iridium, Phosphonium etc.) that are used in the production of Supercapacitors are analyzed, and along with their stroke degradation, we separate the environmentally inert and the environmentally harmful types of Supercapacitors.

A key towards a sustainable future lies both between the exploitation of Renewable Energy Sources (and our ability to capture and store the stochastic power generated) and the R&D of new materials that can be used in this process without disregarding the environmental "leftovers" after their usable period of time. For this reason, this study also emphasizes on the End-of-Life phase of this electric energy storage method.

Keywords: energy storage; end-of-life; capacitors; environment; supercapacitors

INTRODUCTION

The ever changing needs of the world regarding energy demands is shifting towards energy storage. Applications are found in power grids, home energy producers and even electric cars. Supercapacitors are here to bridge the gap between conventional batteries and simple capacitors. Supercapacitors' high surface area electrode materials along with thin electrolytic dielectrics allow them to achieve capacitances much greater than conventional capacitors, thus leading to attainable greater energy densities while maintaining the high power characteristics of conventional capacitors. Research and development (R&D) of these electrode materials and of the electrolytic dielectrics constantly show us the way to upgrading the characteristics of Supercapacitors. This study explores these materials and their characteristics towards environmental issues. A key aspect of this study is to define the recyclability of Supercapacitors according to their materials.

Hierarchical Classification of Supercapacitors

Currently, Supercapacitors can be divided into three general classes [1]:

i. Electrochemical double-layer capacitors (EDLC); it is the combination of two carbon based electrode materials separated by an insulator. The storage of the energy charge takes place by

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non-faradaic manner and there is no charge transfer between electrode and the electrolyte. Carbon materials are unique structures with great surface area, excellent electric conductivity, high chemical stability and high mechanical stability.

ii. Pseudocapacitors; they electrostatically store the charge and the electrode-electrolyte interface manages to transfer the faradaic charge. They have higher specific capacitance and higher energy density than EDLCs. Transition metal oxides and conducting polymers are good examples of materials used in this technology.

iii. Hybrid capacitors

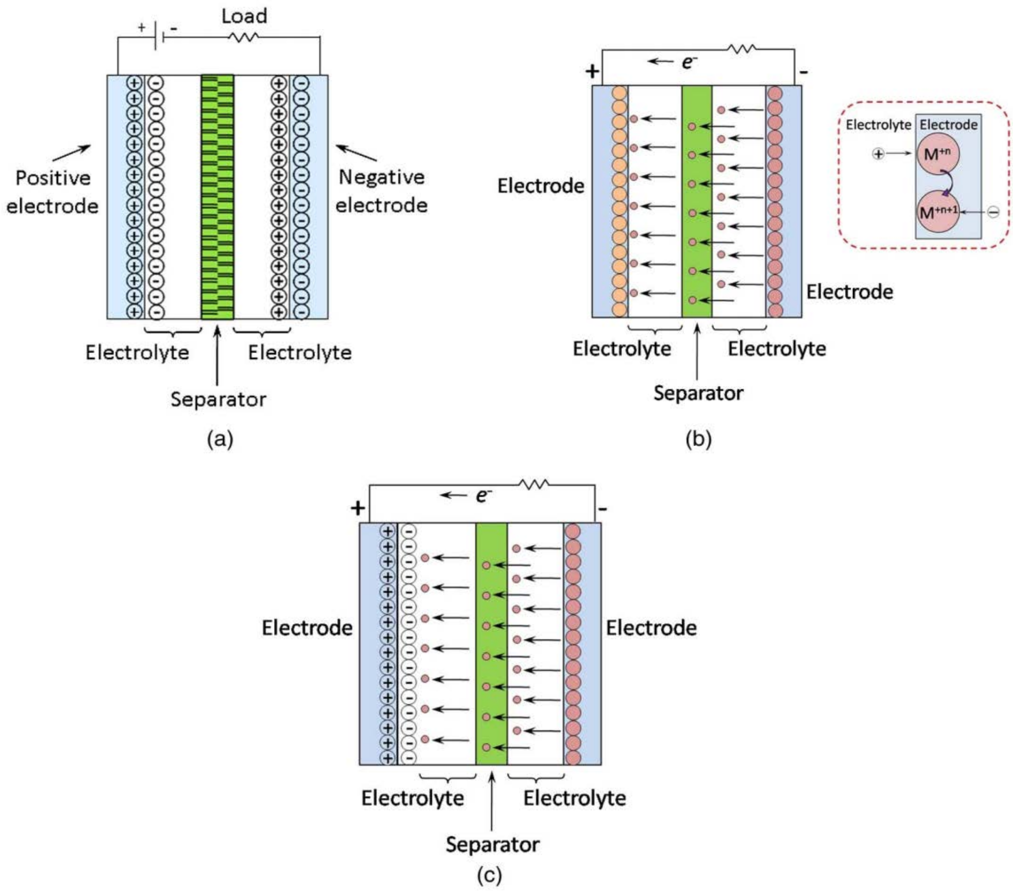


Figure 1: Schematic representation of supercapacitors:
(a) EDLC, (b) Pseudocapacitor, (c) Hybrid [2]

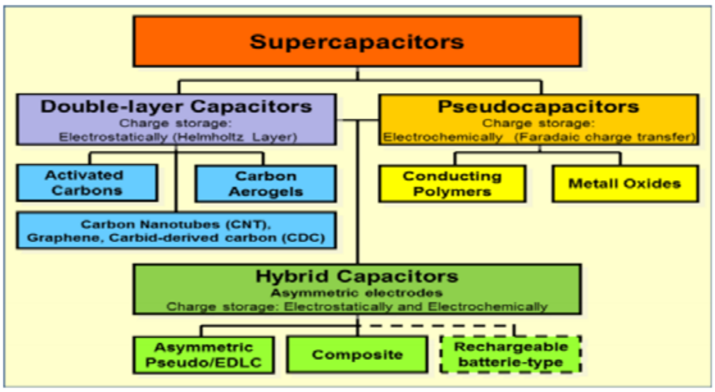


Figure 2: Classification of Supercapacitors [3]

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Electrode Materials Used in Supercapacitors

As seen above, Supercapacitors can be manufactured by various materials. In order to define the environmental concerns of these materials, we should first define these materials. Some of the current materials that can be used, can be found in the table below.

Table 2: List of materials used in Supercapacitors as electrode

Class	Index No	Type	Contains	Ref
Carbon based	i	Single Walled Carbon Nanotubes	C	[1]
	ii	Multiwalled Carbon Nanotubes		
	iii	Fullerene		
	iv	Graphene		
	v	Activated Nanoporous Carbon		
	vi	Activated Carbon Nanofibers		
	vii	Graphene based Nanocomposites		
Metal Oxides	viii	RuO_2	Ru	[1]
	ix	IrO_2	Ir	[4]
	x	MnO_2	Mn	
	xi	SnO_2	Sn	
	xii	$BiFeO_3$	Bi	
	xiii	V_2O_5	V	[1]
	xiv	NiO	Ni	[4]
	xv	$NiFe_2O_4$	NiFe	
	xvi	Bi_2O_3	In	
	xvii	Fe_3O_4	Fe	[1]
	xviii	Co_3O_4	Co	[4]
Conducting Polymers	xix	Polyaniline nanofibers	N	[1]
	xx	Polypyrrole film	N	
	xxi	Poly(3,4-ethylenedioxythiophene) (PEDOT)	S	

Electrolyte Materials used in Supercapacitors

Another very important material used in a Supercapacitor is the electrolyte. The electrolyte defines the performance of the Supercapacitor, as the electrolyte concentration has to be high in order to avoid depletion issues during the charging phase. If the electrolyte reservoir is small compared to the area of the electrode, the performance of the Supercapacitor will be reduced. Gonzalez et al [5] also mention that there are two types of electrolytes used: Aqueous and organic and, ionic liquids. The most recent activated carbon based supercapacitors (SCs) on the market use electrolyte solutions based on aprotic solvents, typically acetonitrile (AN) or organic carbonate-based solvents (propylene carbonate (PC), ethylene carbonate, ethyl methyl carbonate etc.) with cell voltage up to 2.85 V [6]. Another study used an ionic liquid based composite gel polymer electrolyte containing nanostructured SiO_2 [7]. Other different electrolytes can be found in the table below:

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Table 3: Types and Chemical Composition of Electrolytes

Type	Index No	Chemical Composition	Ref
Organic	i	Acetonitrile	[8]
	ii	Propylene Carbonate	[9]
Salt	iii	tetraethylammonium tetrafluoroborate	[10]
	iv	Tetraethylphosphonium tetrafluoroborate	
	v	Triethylmethylammonium tetrafluoroborate	
Ionic	vi	1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (EMI-TFSI)	[11]
	vii	1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4)	
	viii	1-methyl-1-propylpiperidinium bis (trifluoromethylsulfonyl) imide (MPPp-TFSI)	
	ix	1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4])	[12]
	x	1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([BMIM][TFSI])	

As it can be seen, the variety of materials is not limited. New combinations are being studied and tested in order to produce the supercapacitor that fits the current and future energy trends.

Recycling Supercapacitors

Supercapacitors should be recycled according to European Union (EU) Directive 2002/96/EC on waste electric and electronic equipment [13]. Several hazards are needed to be considered in the development of the recycling technologies [14]:

- Hazards associated with the solvents. The most widely used solvents for dissolving electrolytes are propylene carbonate (PC) and acetonitrile (AN).
- Hazards associated with the electrolytes. The electrolytes used in supercapacitors are organic salts. Tetraethylammonium tetrafluoroborate ($TEA\text{-}BF_4$) is the most widely used in commercial supercapacitors.
- Hazards associated with the polymer binder. The most commonly used binders are fluoropolymers such as polytetrafluroethylene (PTFE) or poly (vinylidene fluoride) (PVDF) due to their inert nature.

Jiang and Pickering [14] have also studied the recycling of supercapacitors based on shredding and mild thermal treatment, where they conclude that the three main components of a supercapacitor (activated carbon, solvent and aluminum) can be recycled while the polymer binder and electrolyte salt are left behind in the activated carbon. After shredding, a mild thermal treatment (200^{o}C) can evaporate the solvents in 5 mins.

Vermisoglou et al [15] developed a simple and low-cost method for recycling of supercapacitor material. This method aims in recovering the fundamental metal and carbon components and also deal with the electrolyte by dissolving it in an aprotic solvent in order to avoid hazardous anions.

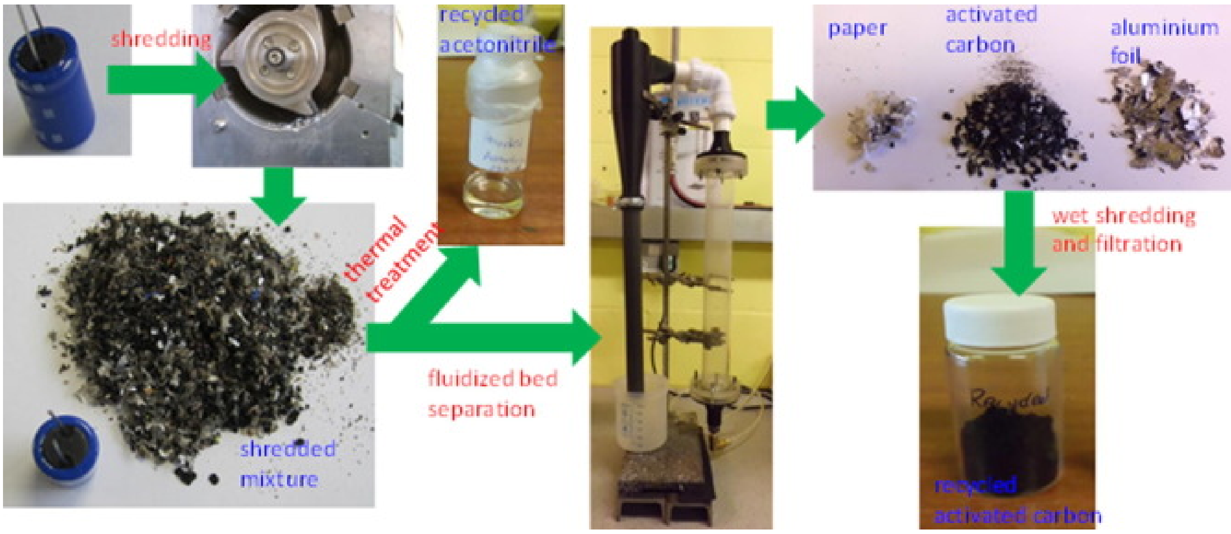


Figure 3: The recycling process ant the separated products from supercapacitors [15]

Toxicity and Environmental issues in Materials used in Supercapacitors

Apart from the recycling process described above, we should also bear in mind the various dangers associated with the handling of materials used in the manufacturing process of supercapacitors. For this reason, the previously noted materials will be classified according to their toxicity and other factors, following the EU Directive 2001/59/EC [16] and the Global Harmonized System of Classification and Labelling of Chemicals.

Although GHS concentrates on human related issues regarding the chemicals, one can clearly see that some of these can damage the aquatic environment with chronic toxicity. The most toxic substance seems to be the 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]) as it is characterized "Very toxic to aquatic life with long lasting effects". In general, the electrodes are environmentally inert, with the exception of Vanadium which is toxic. Special care should be given to the electrolytes, as they can sip easily into the water horizon and damage the environment.

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Table 4: Summary of GHS regarding the materials mentioned in this study [17]

Acute Toxicity	Oral	3	LD_{50} > 50 mg/kg < 300 mg/kg	Toxic if swallowed
		4	LD_{50} > 300 mg/kg < 2000 mg/kg	Harmful if swallowed
	Dermal	3	LD_{50} > 50 mg/kg < 300 mg/kg	Toxic in contact with skin
		4	LD_{50} > 300 mg/kg < 2000 mg/kg	Harmful in contact with skin
Skin Corrosion		1B	Destruction of skin tissue based on exposure of up to 1 hour	Causes severe skin burns and eye damage.
Skin irritation		2	Mean value of $2.3 > 4.0 for erythema / eschar or edema in at least 2 of 3 tested animals from gradings at 24, 48, and 72 hours (or on 3 consecutive days after onset if reactions are delayed); inflammation that persists to end of the (normally 14-day) observation period.	Causes skin irritation
Eye irritation		1	Effects on the cornea, iris or conjunctiva that are not expected to reverse or that have not fully reversed within 21 days	Causes severe eye damage
		2A	Effects on the cornea, iris or conjunctiva that fully reverse within 21 days	Causes severe eye irritation
		2B	Effects on the cornea, iris or conjunctiva that fully reverse within 7 days	Causes eye irritation
Hazardous to the Aquatic Environment	Chronic toxicity	1	$L(E)C_{50} \leq 1.00$ and lack of rapid degradability and/or BCF≥500	Very toxic to aquatic life with long lasting effects
		2	$1.00 < L(E)C_{50} \leq 10.0$ and lack of rapid degradability and/or BCF≥500	Toxic to aquatic life with long lasting effects
		3	$10.0 < L(E)C_{50} \leq 100$ and lack of rapid degradability and/or BCF≥500	Harmful to aquatic life with long lasting effects
		4	No acute toxicity and lack of rapid degradability and BCF≥500	May cause long lasting harmful effects to aquatic life
Germ Cell Mutagenicity		2	Cut-off/concentration limit: ≥1.0%	Suspected of causing genetic defects
Reproductive Toxicity		2	Cut-off/concentration limit: ≥0.1%	Suspected of damaging fertility or the unborn child
Specific Target Organ toxicity	Repeated Exposure	1		Causes damage to organs through prolonged or repeated exposure
	Single Exposure	2		May cause damage to organs through prolonged or repeated exposure
		3		May cause respiratory irritation Or May cause drowsiness or dizziness

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Table 5: Electrolytes toxic and other documented environmental issues

Type	Index No	CAS #	Acute Toxicity	Skin Irritation	Skin Corrosion	STOT RE	Eye Irritation	Aquatic Chronic	Other Info
Organic	i	75-05-8	4				2		Highly Flammable liquid and vapor, Harmful if swallowed, in contact with skin or If inhaled
	ii	108-32-7					2		
Salt	iii	429-06-1	4	2			2		
	iv	665-49-6	No Data Available						Corrosive, Irritant
	v	69444-47-9	No Data Available						Harmful, Corrosive, Irritant
Ionic	vi	174899-82-2	3		1B			2	Toxic if Swallowed or in Contact with Skin, Causes Severe Skin Burns and eye damage
	vii	143314-16-3	4					2	
	viii	608140-12-1	No Data Available						
	ix	174501-65-6	3	2			1	1	
	x	174899-83-3	3		1B	2		2	Toxic if Swallowed or in Contact with Skin, Causes Severe Skin Burns and eye damage, Dangerous for the environment

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Table 6: Electrodes toxic and other documented environmental issues

Class	Index No	CAS #	Acute Toxicity	STOT RE	STOT SE	Eye Irritation	Eye Damage	Germ Cell Mutagenicity	Reproduction	Aquatic Chronic	Other Info
Carbon based	i		Inert / No Data Available								
	ii		Inert / No Data Available								
	iii	99685-96-8			3	2					
	iv		Inert / No Data Available								
	v		Inert / No Data Available								
	vi		Inert / No Data Available								
	vii		Inert / No Data Available								
Metal Oxides	viii	12036-10-1	Inert / No Data Available								
	ix	12030-49-8	Inert / No Data Available								
	x	1313-13-9	4								
	xi	18282-10-5	Inert / No Data Available								
	xii		Inert / No Data Available								
	xiii	1314-62-1	4				1	2	2	2	Toxic and dangerous for the environment
	xiv	1313-99-1		1						4	may cause cancer by inhalation
	xv	12168-54-6	No Data Available								Toxic, May cause cancer by inhalation
	xvi	1304-76-3	Inert / No Data Available								
	xvii	1317-61-9	Inert / No Data Available								
	xviii	1308-06-1								3	May cause allergy or asthma symptoms or breathing difficulties if inhaled
Conducting Polymers	xix		Inert / No Data Available								
	xx		Inert / No Data Available								
	xxi		Inert / No Data Available								

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Conclusions

Supercapacitors are an emerging technology for both mobile and stationary applications. The materials used in their manufacturing process include both environmentally inert and toxic substances. Usually the electrolyte poses a threat towards the environment and needs to be tended with care in the process of recycling. The method that is dominant at the moment is the shredding of supercapacitors and the recovery of their materials.

References

[1] Chen, S-M., Ramachandran, R., Mani, V., Saraswathi, R. (2014). Recent Advancements in Electrode Materials for High-performance Electrochemical Supercapacitors: A Review. International journal of Electrochemical Science, 9, 4072-4085

[2] Vangari, M., Pryor, T. and Jiang, L. (2013). Supercapacitors: Review of Materials and Fabrication Methods. Journal of Energy Engineering, 139(2), 72-29

[3] Gidwani, M., Bhagwani, A. and Rohra, N. (2014). Supercapacitors: the near Future of Batteries. International Journal of Engineering Inventions, 4(5), 2-27

[4] Lockhande, C.D., Dubal, D.P. and Joo, O-S. (2011). Metal Oxide thin Film Based Supercapacitors. Current Applied Physics, 11(3), 255-270

[5] Gonzalez, A., Goikolea, E., Barrena, J.A. and Mysyk, R. (2016). Review on Supercapacitors: Technologies and materials. Renewable and Sustainable Energy Reviews, 58, 1189-1206

[6] Jänes, A., Eskusson, J., Thomberg, T., Romann, T., lust, E. (2016). Ionic liquid-1,2-dimethoxyathane mixture as electrolyte for high power density supercapacitors. Journal of Energy Chemistry, Available online 16 February 2016, ISSN 2095-4956, http://dx.doi.org/10.1016/j.jechem.2016.02.011

[7] Ortega, P., Trigueiro, J.P.C., Silva, G.G., Lavall, R.L. (2016). Improving supercapacitor capacitance by using a novel gel nanocomposite polymer electrolyte based on nanostructured SiO_2, PVDF and imidazolium ionic liquid, Electrochemica Acta, 188, 809-817

[8] Cheng, F., Yu, X., Wang, J., Shi, Z., Wu, C (2016). A novel supercapacitor electrolyte of spiro-(1,1')-bipyrolidinium tetrafluoroborate in acetonitrile/dibutyl carbonate mixed solvents for ultra-low temperature applications. Electrochemica Acta, 200, 106-114

[9] Pohlmann, S., Olyschläger, T., Goodrich, P., Vicente <J.A., Jacquemin, J., Balducci, A. (2015). Mixtures of Azepanium Based ionic Liquids and Propylene Carbonate as High Voltage Electrolytes for Supercapacitors. Electrochemica Acta, 153, 426-432

[10] Su, D.S. and Centi, G. (2013). A perspective on carbon materials for future energy applications. Journal of Energy Chemistry, 22(2), 151-173

[11] Li, J., Tang, J., Yuan, J., Zhang, K., Shao, Q., Sun, Y., Qin, L-C. (2016). Interactions between graphene and ionic electrolyte in supercapacitors. Electrochemica Acta, 197, 84-91

[12] Tamailarasan, P. and Ramaprabhu, S. (2012). Carbon nanotubes-graphene-solidlike ionic liquid layer-based byrid electrode material for high performance supercapacitor. The Journal of Physical Chemistry, 116, 14179-14187

[13] EUROPEAN UNION (2013). Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE) - Joint declaration of the European Parliament, the Council and the Commission relating to Article 9 [Online] Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32002L0096 [Accessed: 28.04.2016]

[14] Jiang, G. and Pickering, S.J. (2016). Recycling supercapacitors based on shredding and mild thermal treatment. Waste Management, 48, 465-470

[15] Vermisoglou, E., Giannouri, M., Todorova, N., Giannakopoulou, T., Lekakou, C., Trapalis, C. (2016). Recycling of Typical Supercapacitor Materials. Waste Management & Research, 34(4), 337-344

[16] EUROPEAN UNION (2001). Commission Directive 2001/59/EC of 6 August 2001 adapting to technical progress for the 28th time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (Text with EEA relevance.). [Online] Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1462202401591&uri=CELEX:32001L0059 [Accessed: 28.04.2016]

[17] United Nations (2013). Globally Harmonized System of Classification and labelling of Chemicals, Fifth Revised Edition [Online] Available at: https://www.unece.org/fileadmin/DAM/trans/danger/ publi/ghs/ghs_rev05/English/ST-SG-AC10-30-Rev5e.pdf [Accessed: 28.04.2016]

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Citizen’s mentality and behaviour regarding household pharmaceutical waste

A. Zorpas[1*], M. Demitriou[1], I. Voukkali[2]

[1] Cyprus Open University, Faculty of Pure and Applied Sciences, Environmental Conservation and Management, Laboratory of Chemical Engineering and Engineering Sustainability, Nicosia, Cyprus
[2] I.E.S.T - EnviTech Ltd, (Institute of Environmental Technology and Sustainable Development, Department of Research and Development) www.envitech.org, Paralimni, Cyprus
* Corresponding author: Email: antonis.zorpas@ouc.ac.cy

Abstract

The disposal of unused or expired pharmaceuticals via the sink or the toilet or in the household waste is considered to be one of the main pathways for emission of pharmaceuticals into the environment. Through this paper we are aiming (a) to determine the attitude of citizens in Cyprus regarding the disposal of pharmacies, (b) to investigate if a centralized waste management system can be established (c) as well as to identified the main reasons why those waste are produced. The result indicted that in Cyprus there is lack of data regarding the amount of pharmaceutical waste that are discarded into household waste and sinks. From the survey audit 86.6% of men’s and 83.3% of women’s were used pharmacy / drug with or without doctor’s recipe. The main reason that pharmaceutical are produced is due to the social behaviour. Moreover, it is estimated that citizens mainly keep unused medicines at home in case they're needed again as well as patients use to cut-off or to reduce their treatment. The main disposal solution of unused or expired medicines remain the household bin and sewage system (sink or toilet).

Keywords: *pharmaceutical waste management; social attitude; social behavior; drugs; hazardous waste*

1. INTRODUCTION

Pharmaceuticals were first discovered in the environment around 40 years ago [1] and are produced and used in increasingly large volumes from year to year. A wide range of pharmaceuticals has been found in fresh and marine waters, and it has recently been shown that even in small quantities, some of these compounds have the potential to cause harm to aquatic life [2]. Several research’s has been done, focuses on the trace levels of pharmaceuticals in environmental samples, including sewage effluent, surface water, groundwater, and even drinking water, mainly in EU countries, which results in their continuous release into the environment [3, 4]. Nowadays according to Rizzo et al., [4] a wide range of trace chemical contaminants persisting in municipal wastewater after conventional treatment and includes among others inorganic compounds, persistent organic pollutants like endocrine disrupting compounds, pharmaceutically active compounds and many others complex compounds which all those are consider to be an important and significant environmental issue. One of the main reasons that pharmaceutical products (Figure 1) produce waste which creates significant negative issue to the environment is the social attitude and more specific about what is consider as the best practise to dispose of, those wastes. Several researches indicated that the most wide and known method is to dispose unused medications by flushing them down the toilet or discarding them in the garbage [5].

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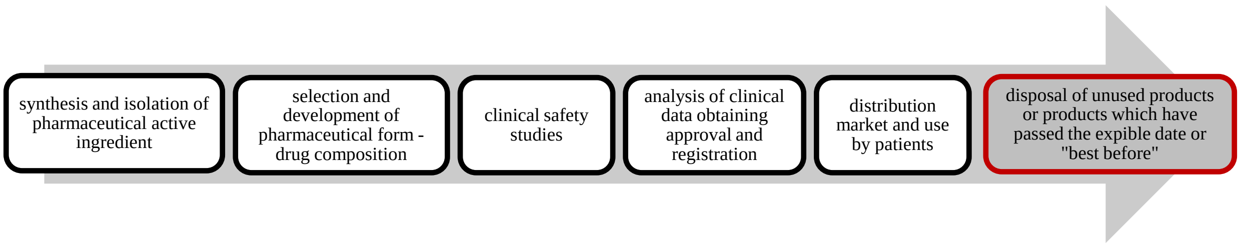


Figure 1: Life cycle analysis of pharmaceutical products

The problem of pharmaceutical waste is very complex. On one hand, are the negative issues which affect the environment as mentioned above and on the other, are the reasons that those wastes produced. Cyprus according to Eurostat is considered to be the first EU country in the use of antibiotics and drugs with or without doctor recipe. In 2013, the consumption of antibiotics for systemic use in the community ranged from 10.8 defined daily doses (DDD) per 1000 inhabitants/day (the Netherlands) to 32.0 DDD per 1000 inhabitants/day (Greece); a 2.9-fold difference, which is similar to previous years. The population-weighted EU/EEA mean consumption was 22.4 DDD per 1000 inhabitants/day, representing a continuing increase over the last five years for the EU as a whole, as well as for six individual countries [6].

Cyprus pharmaceutical industry today consists of six industrial plants which mostly produce generically pharmaceuticals. According to the official statistics from Cypriot pharmaceutical industry during 2012 has been placed on the international market pharmaceutical products which worth more than 220 m €. Those products, corresponds approximately 34% of the domestic exports. On 2010 the exports of drugs from Cyprus (mainly to EU countries, while smaller quantities to Middle East and Africa) was more than 23% of the total production. In the free part of the Island exists 85 licensed drug distributors, 478 private and 41 governmental pharmacies (which based in hospitals and other health care services). According to the Statistical Services on 2011 the total spending on health care was up to 7.2% of the GDP of the country while on 2014 were up to 8.1%. In the private sector on 2011 the total expenses focuses on pharmaceutical products were 149.6 m € while on 2014 were more than 160 m € [7]. On the other hand the governmental sector of health care (including hospitals etc) spend more than 110 m € / year for pharmaceutical products. According to Fent [8] many countries are not in a position to provide reliable data regarding the health care sector. The last health care report carrying on 2008 from the EU health care sector [7] estimated that, the use of prescribed medicines was up to 37.5% of the total population, on which 42.1% was women and 32.6% was men. It is generally observed from the same report that the rate of use of prescription drugs increases with age, with the exception of children up to four years which exhibit disease with a greater frequency. The most common drugs were those for hypertension, cholesterol, painkillers, diabetes, stomach problems, and antibiotics [7]. It is important to mentioned that Cyprus ranks second behind Greece in European level on the use of antibiotics, indicated that Cypriots use antibiotics in non-rational way with consequent effects of increasing antimicrobial resistance and diffusion of multi-resistant bacteria that expose the safety of the population [9]. According to Hatjimichael et al., [10] the amount of antibiotics that are used in Cyprus is higher than those in Sweden, Norway and Denmark and these is because of the presents of polypharmacy phenomena due to the influence of demographic and socio-economic factors.

This paper focuses on the investigation for effective implementation of an appropriate pharmaceutical waste management system from domestic sectors in Cyprus. The development and implementation of a management system for medical waste will contribute substantially to solving the problem of irrational and uncontrolled disposal of drugs. Moreover through this research we are aiming to determine the attitude of citizens in Cyprus regarding the disposal of pharmacies/drugs, and to investigate if a centralized waste management system can be established as well as to identified the main reasons why those waste are produced.

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2. MATERIALS AND METHODS

The problem of safe disposal of unused and expired medicines and drugs from households in Cyprus is largely unknown. Until now there is no any specific management system in place focus on pharmaceutical waste. This creates confusion to the citizens on what and which is considering to be the most environmental friendly methods. Moreover, through this research some other goals had been set including (i) the identification of the reasons that those waste are produced; (ii) to record existing disposal practices from citizens; (iii) to investigate the intention of participation of citizens in activities organized collection and safe management of waste medicines and (iv) to identifying several socioeconomic factors which influence the perceptions, knowledge, attitudes / practices of citizens in relation to the safe disposal of pharmaceutical waste in the environment. The sample of 184 citizens consists of adults and cover all age groups from the age of 18+ and were living to the District of Nicosia (covering urban and rural areas). For the pilot survey the method of convenience sampling were used. This method was chosen due to specific advantages over other methods shows in terms of ease of access issues in information management and the time available for data collection and is usually applied where there is no direct access to a representative sample and highly exploratory surveys can give valuable but empirical results with generalizability to populations with similar characteristics to those of the sample [11]. The survey was caring out using 184 citizens (44.6% men's and 55.4% women's) from several target groups, educated background, ages and economical activities. 6% from the age less than 20, 40.8% from the ages of 21-40, 31.5% from the ages of 41-60, 21.7% from the ages of 61-80. 67.7% of those were leaving in more urbanized areas and 32.4% in peri-urban areas (mostly in small villages). 51.3% of the responders have a university education while 24.0% were holders of postgraduate or doctoral degree, followed from the 27.3% that were graduates of academic colleges and 20.8% were graduates of higher vocational schools while 27.9% were high school or high school graduates. Finally, 41.8% of respondents were employed in the public and broader public sector, 22.3% in the private sector, 12.5% were retired, 7.1% self-employed, 6.0% housewives, 5.4% students and 4.9% were unemployed. It is important to know that the characteristics of the sample are close to the actual distribution of the population in Nicosia. A specific questioner was used divided in several sections with specific characteristics: demographic and socioeconomic characteristics**,** level of knowledge regarding the risks posed by the use of drugs, level of knowledge regarding the disposal methods of unused of drugs**,** participation declaration of intent in case of application program suitable collection and safe disposal of pharmaceutical waste, environmental issues, and social issues. The statistical analysis were caring out using the Statistical Package for Social Sciences (SPSS V.22.0).

3. RESULTS AND DISCUSSIONS

The problem of pharmaceutical waste in the framework of compositional analysis is complete unknown. According to Zorpas et al., [12] (Figure 2) during the compositional analysis of household's waste exist a waste stream called "other wastes" which is about 8% (more or less) of the total household wastes and a range from 15-45% of those "other wastes" consist the pharmaceutical waste. Due to the absence of any awareness activity regarding the problems that are created from the uncontrolled disposal of those wastes, citizens use to disposed-off anywhere, but the most preferable "technique" is in the toilet and in the garbage. A typical pharmaceutical compositional analysis according to Filippis et al [13] includes active ingredients; excipients are added as binders in the manufacture of drugs and packaging materials such as paper, cardboard, plastic, aluminum and glass. This analysis is line with the forms that pharmacies is in the market and includes solid phase, semi solid and liquid phase. Also, according to Pratyusha et al. [14] pharmaceutical waste consist from two main streams.

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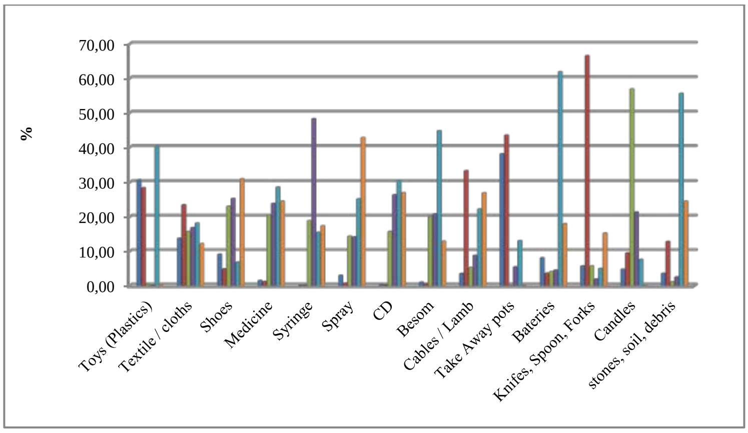
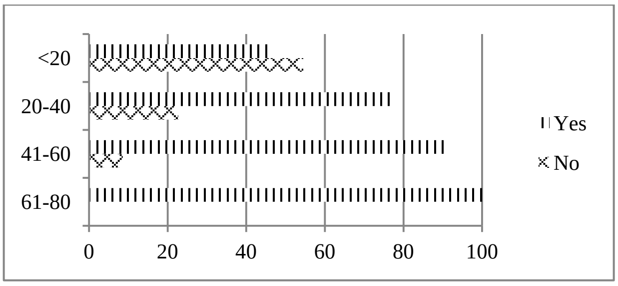


Figure 2: Other waste stream compositional analysis regarding the household wastes

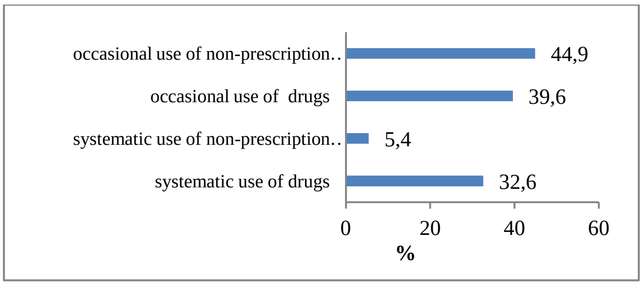
The first are come from internal health care and the second from hospitals. Mainly pharmaceutical waste consist expiable drungs, drungs that we use to keep but not needed any more and are not expiable, package materials which contain or not drugs, plasters, syringes, needles, intravenous drug tubes etc. According to WHO [15] pharma-ceu-tical wastes are considered to be all the waste from pharmaceutical products and include expired and unused medi-cations, prescription or not as well as packaging such as bottles, flasks and boxes still containing pharmaceutical residues. The use of drugs is strongly related with the ages as indicated the survey audit and Musson et al [16]. 84.8% of the participants have used drugs during the last 12 months compared with 15.2% who said he has not used (Figure 3a). The majority of the participants (44.6%) mentioned that they have made occasional use of non-prescription drugs, while 39.1% indicated that they have done occasional use of prescription drugs (Figure 3b). The main basic classes of drugs that the participants occasional or regular used indicated in Figure 3c. 65.8% were used painkillers and anti-inflammatory, 38.6% were used antibiotics, (with or without any doctors recipes) and 20.1% other medicines for fever. Similar results are presented and from others researches [17]. In order to build up a strategy focus on management on pharmaceutical waste management we must first identified the reasons why those waste are produced. Through this survey, 76.8% of the participants indicated that they keep remaining quantities of unused drugs after their medical treatment. Through the survey the main reasons that pharmaceutical wastes are produced has to do with the participant's behaviour in relation with how they understand and accept medical treatment and ethical issues. Those reasons are (i) the improvement of the patient's health (71.2%) (Figure 4a). In that case patients used to cut-off their treatment after the first 3-4 days and they don't complete their medical treatment; (ii) change of medication due to misdiagnosis or adverse side effects (65.8%); (iii) buy more drugs than those needed; (iv) changing the dosage of the drug (42.9%), followed by smaller amounts with or without any advice from their doctor; (v) difficulties in the application of the drug package (vi) in case the patient dies (vii) the expiration date of the drug. Similar results were observed and other studies caring out before [18]. Also 46.2% obtained by the change of the medication due to incorrect diagnosis, 44.6% by the supply quantity of more drug than required. Furthermore 93.5% (Figure 4b) continue keep several drugs in case they will need them again (which believes that they can use them in case they will present similar symptoms with the last time). This phenomenon is also mentioned from Vellinga et al., [19]. An important result from this research was the fact that 1.6% of the participants afraid that may cannot find the same drugs in the market and they keep unnecessary quantities into the house.

According to the survey audit 66.8% of the participant, know that the drugs beyond their beneficial effects are a threat to the environment. However the majority of the total sample (73.9%) mentioned that "did not know whether drugs have been detected in surface and groundwaters". Moreover, 70.1% mentioned that they did not know whether drugs have been detected in drinking water. 67.9% of the participant links the uncontrolled use of antibiotics by developing antimicrobial resistance. Finally a question whether the rejection medicines in the trash, the sink or the toilet has negative impacts on the environment, 52.7% gave a positive answer, 38.0% said not sure and 9.2% answered negatively.

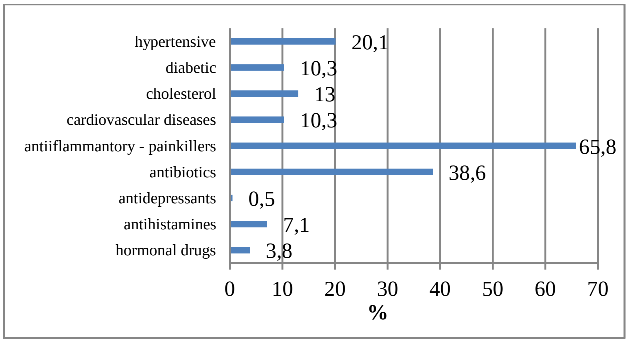
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a



b

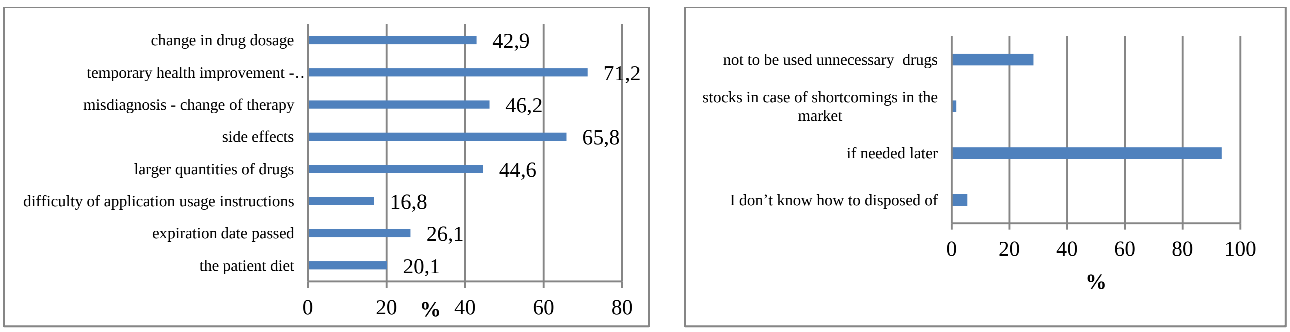


c

Figure 3: (a) Population analysis regarding the use of drugs (b) Population analysis the systematic or occasional use of prescription or non-prescription drugs (c) the most common drugs that are been used from the participants

Regarding how often the participants dispose of expired and unused drugs that keep in their homes, 61% of them mentioned that they used to disposed of one a year while 35% of them 2-3 times per year (Figure 5a). Langley et al [17] mentioned that, in the social context, it is unclear how much unused medicines are disposed of through normal household refuse and domestic sewerage systems. However, 92.4% of the participant in this survey, mentioned that they have chosen to rejects the unused and expired drugs to the bins with other household wastes (Figure 5b) following by the sewage (24.5%), which is consider to be the second most favourable method.

An extremely important result was the fact 8.2% of the responded mentioned that gives the unused drugs to their friends or to the family considering that possibly are useful. Moreover, 85.1% of the participants mentioned that solid drugs are disposed of in the household waste while the liquid drugs into the sewage. In Taiwan, 88% (about 2.6 tons) of unused and expired medications are flushed down the toilet or discarded as regular household trash, causing severe environmental contamination [18]. More specific the same report indicated that 77% of the respondents reported that they discarded their medications at home [directly into trash bins (72%), sinks (2%), toilets (1%), and other places (2%)] and the remaining, 23% returned their unused medications to the pharmacy for disposal (14% to hospital pharmacies and 5% to community pharmacies, 1% to clinic, 1% to cosmeceutical store, 1% to Health Bureau,1% others). Disposal of unused medicines into domestic waste may also lead to landfill leachate and create environmental problems [2].



a b

Figure 4: Main reasons that participants keep medicines / drug at home

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Similar issues may arise with a variety of personal care products which frequently contain biologically active compounds. Also, there are many researches indicated that the most common disposal methods in household level is the sewage, sink and household waste [18, 19]. Vellinga et al [19] mentioned that the most common method in Ireland is via household waste (51%) followed by the sink (29%) and finally in the toilet (14%). 72% of the participants in the survey caring on by Vellinga et al (2014) agree that disposed of their medicine in an environmentally inappropriate way. Moreover the same report identified that older people and medical card holders are significantly more likely to appropriately dispose of unused medicine.

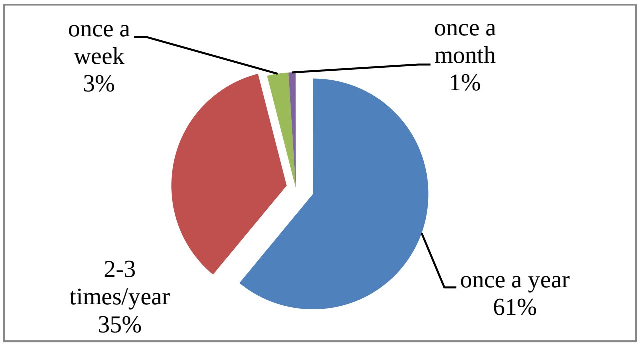


Figure 5a: Frequency rejection of expired or unused drugs

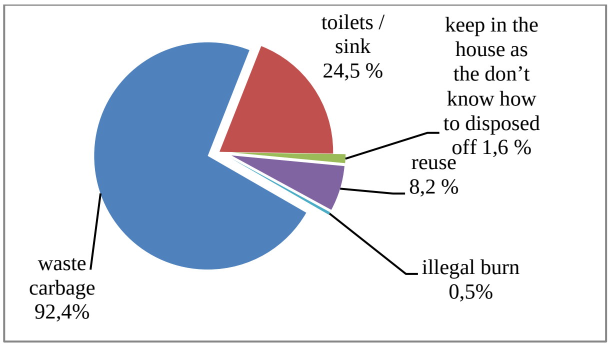
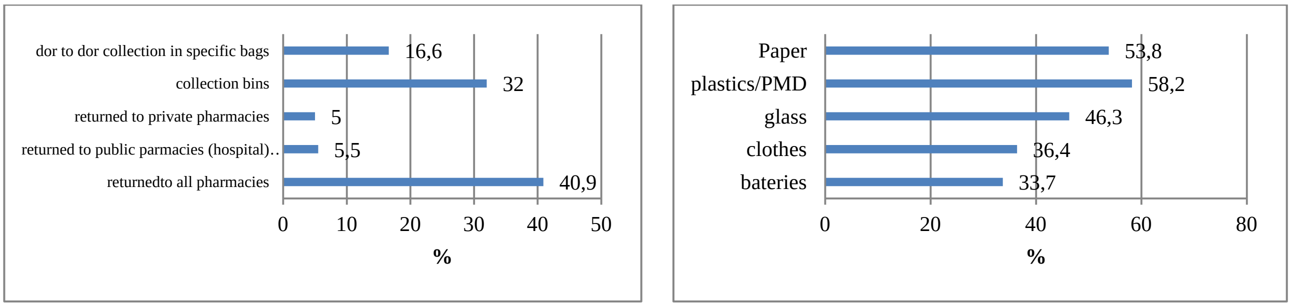


Figure 5b: Most favarable disposal practice of unused and expired medicines at household level from citizens.

Figure 6a shows that the participants will support a pharmaceutical waste management system if exist in place. 40.9% indicated that they are willing to collect and returned in all pharmacies unused or expiable dugs as well as 32.0% are willing to used specific bins (in the concept of recycle bins) if those placed in supermarkets, malls or other centralized areas. 33.7%-58.2% of the participants mentioned that are participated in recycle program (Figure 6b). An important result of the survey was that they are willing to cover part of the cost of the above proposed methods. This cost were varied from 0.05 € to 1 € (38.7% indicate that they are willing to paid 0.10€, 27.4% the amount of 0.05€, 14.5% the amount of 0.25€, 11.3% the amount of 0.50€ and 8.1% 1€).



a b

Figure 6: (a) Main proposed disposal methods regarding pharmaceutical waste (b) participation of the participants in the existing recycling program

Also the respondents consider that the statement of safer practices for disposal of medicines in packaging will help to reduce the presence of pharmaceutical compounds in the environment, the majority replied in percentage 45.1% that this will be extremely helpful, 29.6% very help full, 19.8% moderately and 7.7% to a small extent. Langley et al. [17] indicated that the most commonly cited reason for medicines return was alteration to the medication regime made by the prescriber. This could result from a number of situations including adverse drug reactions, patient led discontinuation, lack of clinical need and the tailoring of new and existing therapies to individual

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patients needs. In Australia the drugs for cardiovascular diseases are the most common group of drugs among those returned to pharmacies which shows that the higher costs of unused medications derived mainly from patients which follows lengthy treatments [20] .

Although the absence of a specific management plan is consider to be an issue, however, the implementation of prevention activities and public awareness event regarding, negative impact on the environment of the uncontrolled disposal of the pharmaceutical waste, negative issues to the health that are created using medicines and drugs without doctors advise and safe disposal methods of waste, will be very useful for the population and for the protection of the environment.

There are many prevention activities [12] similar to the others wastes that can be applied which included into a prevention strategy plan or zero waste strategy plan. Those activities according to several researches [12, 21, 22] includes among others (i) awareness event focuses in specific target groups like, primary and secondary schools local authorities, pharmacies, doctors union etc; (ii) specific guidance's focuses on how people must treat their pharmaceutical wastes, into several economic sectors. For example in household level the collection of those wastes and returned them to the pharmacies or to the doctors or to the hospital could be one option. Also as hospitality industry plays significant rule in the waste production in all level (often pay little attention to their environmental responsibilities) could guide their customers to collect in separated bin their personal pharmaceutical waste than to reduce them into the sewage. Moreover, in each visit to any of the health care sector could be informed with a specific leaflet, indicated the best available practices that exist. Hence, pharmaceutical industries could established collection system of unused drugs, as well as to offer to consumer-patients fewer options for non-prescription drugs and to offer packages with less amounts of drugs and also to introduced instructions on packages for the most environmental disposal methods. Pharmacist must also, cooperated with Local Authorities for the establishment of a collection schemes regarding the expired and unused drugs.

4. CONCLUSION

Most of the participants regardless of gender, age and educational level seem to agree with the view that health sector can play a key role in the rational use of medicines. This research highlights the problems that exist in Cyprus regarding the common practices that are used concerning the pharmaceutical waste. Through this research is indicated that the awareness of the consequences of environmental pollution from the residues of drugs/medicines is related with various demographic and social factors. Furthermore, the investigation showed that there is a positive intention by the citizens for participation in a *drug* take-back program suitable for the safe environmentally management of household pharmaceutical waste. On the contrary the results also showed that there is no corresponding positive intention from the participants to contribute financially for the operation of such a system. Also, there are several methods that can be used to solve the problem of the disposal of unused medicines, and patient education is considered to be the most important one. Patient education should include adequate drug information for patients to safely and effectively use the medication and prevent the waste of medical resources.

References

[1] Bound P.J., Kitsou K., Voulvoulis N., 2006. Houcehold disposal of pharmaceuticals and perception of risk to the environment. *Environmental Toxicology and Pharmacology,* **21,** 301-307.

[2] Bound P.J., Voulvoulis N., 2005. Household Disposal of Pharmaceuticals as a Pathway for Aquatic Contamination in the United Kingdom. *Environmental Health Perpsectives,* **113(12),** 1705-1711

[3] Kolpin DW., Furlong ET., Meyer M., Thurman EM., Zaugg SD., Barber LB., 2002. Pharmaceuticals, hormones and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. *Environ Sci Technol* **36,**1202–1211.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[4] Rizzo L., Manaia C., Merlin C., Schwartz T., Dagot C., Ploy M.C., Michael I., Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for antibiotic resistant bacteria and genes spread into the environment: A review. *Science of the Total Environment* **447,** 345–360

[5] Trach V.A., Brown M.C., Pope N., 2013. Consumer perceptions about a community pharmacy-basedmedication take back program. *Journal of Environmental Management* **127,** 23-27

[6] ECDPC 2014. European Center for Disease Prevention and Control - European Antibiotic Awareness Day. *Summary of the latest data on antibiotic consumption in the European Union.* Pp1-12

[7] Στατιστική Υπηρεσία, 2014. Ευρωπαϊκή Έρευνα Υγείας, 2008. Διαθέσιμο στο: <http://www.mof.gov.cy/mof/cystat/statistics.nsf/0/64eba5dd78134f35c22577d90037a035?OpenDocument&sub=3&sel=1&e=&print&Click=> [Πρόσβαση: 20 Σεπτεμβρίου 2015].

[8] Fent K., Weston A. A., and Caminada D., 2006. Ecotoxicology of human pharmaceuticals. *Aquatic Toxicology*, **76,** 122–159.

[9] ECDC Annual Epidemiological Report, 2010. European Surveillance of Antimicrobial Consumption (ESAC).

[10] Hadjimichael C., Georgiou K., Samoutis G., Demetriades E., 2006. Sales of systemic anti-infective agents in Cyprus in comparison with four other European countries *Pharmacy World and Science* **28 (3),** 135-139

[11] Demitriou M. 2015. Pharmaceutical Waste Management. Dissertation Thesis, Cyprus Open University

[12] Zorpas A., Lasaridi K., Voukkali I., Loizia P., Chroni C., 2015a. Promoting Sustainable Waste Prevention Strategy Activities and Planning in Relation to the Waste Framework Directive in Insular Communities, *Environ. Process.* **2** S159–S173

[13] Filippis De P., Caprariis, De B., Scarsella M., and Verdone N., 2012. Energy recovery from unused and expired medicines. *Waste Management and the Environment VI*.

[14] Pratyusha K., Gaikwad M. N., Phatak A. A., and Chaudhari P.D., 2012. Review on: Waste Material Management in Pharmaceutical Industry. *Int. J. Pharm. Sci. Rev. Res.*, **16(2),** N° 27, 121-129.

[15] World Health Organization (WHO), 2013. Safe management of wastes from health-care activities. 2nd edition.

[16] Musson E. S., Townsend T., Seaburg K., and Mousa J., 2007. A Continuous Collection System for Household Pharmaceutical Wastes: A Pilot Project. *Journal of the Air & Waste Management Association*, **57,** 828–835.

[17] Langley *Z* C., Marriott J., Mackridge A. and Daniszewski R., 2005. An analysis of returned medicines in primary care. *Pharm World Sci*, **27,** 296–299.

[18] Chien Y. H., Ko J.J., Chen Y.C. Weng H. S., Yang C. W., Chang C. Y., Liu P. H., 2013. Study of Medication Waste in Taiwan. *J Exp Clin Med*, **5(2),** 69-72.

[19] Vellinga A., Cormicana S., Driscoll J., Furey M., O'Sullivan M., and Cormican M., 2014. Public practice regarding disposal of unused medicines in Ireland. *Science of the Total Environment,* **478,** 98–102

[20] Guirguis K., 2010. Medications collected for disposal by outreach pharmacists in Australia. *Pharm World Sci*, **32,** 52–58.

[21] Kümmerer, 2010. Pharmaceuticals in the environment. *Annual review of environment and resources*, **35,** 57–75.

[22] Daughton, G. C., and Ruhoy S. I., 2009. Environmental footprint of pharmaceuticals: the significance of factors beyond direct excretion to sewers. *Environmental Toxicology and Chemistry*, **28(12),** 2495-2521.

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Energy efficiency assessment of gasification plant using hazardous/non-hazardous industrial wastewater treatment sludge

G. Yildiz Töre*, Y. B. Kar

Department of Environmental Engineering, Namık Kemal University, 59860, Çorlu, Tekirdağ, Turkey
*Corresponding author: Email: gyildiztore@nku.edu.tr

Abstract

In this study; moisture, ash and heating values of treatment sludge samples taken from wastewater treatment plant dewatering units of textile, dairy, vegetable and non-vegetable oil, glass and metal industries located in Thrace Region of Turkey, were measured and the best proper feeding sludge combinations, on the basis of significant parameters in terms of gasification yields were identified for a downdraft fluidised bed reactor running on a pilot scale plant. In addition, the same measurements were performed on the char and cyclone dust samples that occurred as a result of gasification process and energy yields of the combinations have been determined. According to sludge characterization results, after gasification, the char and cyclone dust samples were measured between 800-3500 $kcal.kg^{-1}$ and 500-900 $kcal.kg^{-1}$, respectively and it was understood that especially the char samples, having high heating values, can be re-processsed in this thermal process before disposal to landfill. Furthermore, it is observed that sludge combination, which has high calorific value and low ash ratio, had the highest energy efficiency compared to the other sludge combinations. So, if the proper sludge combination can be prepared, gasification process can be the best industrial sludge management method for this region both industrial sludge minimisation and energy recovery before landfill.

Keywords: gasification; energy efficiency; industrial sludge; char and cyclone dust; thermal treatment

1. INTRODUCTION

Today waste disposal and energy obtained by the gasification technology has become an important issue. Gasifcation is a suitable technology because it reduces waste volume, removes toxic organic compounds and fixes heavy metals in the resultant solid. The gasification process converts any carbon containing material into a combustible gas (Syngas) composed primarily of carbon monoxide, hydrogen and methane, which can be used as a fuel to generate electricity and heat, and a little amount of these gases can be used to dry wet sewage sludge. Typical raw materials used in gasification are coal, biomass, agricultural wastes, sewage sludge, and petroleum based materials. The product gas from these materials is a mixture of non-condensable gases, such as CO, CO_2 and H2, and light hydrocarbons, such as CH_4, C_2H_4, C_2H_6, C_3H_8 and C_3H_6. Their relative proportions depend on the pyrolysis reaction conditions, temperature, heating rate, fuel moisture content, particle size, composition of ambient atmosphere, pressure and vapor residence time [1-4]. Gasification is regarded as a prospective and promising method for rendering sewage sludge (an example of unconventional biomass) harmless [5-8]. Unfortunately, apart from the valuable gas fuel produced, the process results in solid and liquid waste by-products [9-11]. The solidification of mineral substances during gasification produces solid products, mostly ash, but also char coal in some cases [5,6]. The formation of the latter depends on the composition of nonflammable

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inorganic substances in the sludge which considerably decreases the Debye characteristic temperatures of the ash [10]. Liquid products, i.e., tar, as a result of the condensation of the contaminants present in gas [11]. On the other hand, based on previous studies in the literature, water content (dry matter content) could affect gas yields, gas compositions, and char yields, among others, during biomass conversion in sub- and supercritical water. However, sewage sludge is different because of the complicated water forms contained, including free, interstitial, and surface and bound water [12]. Although the water content in sludge decreased after mechanical dewatering (lost most of free water), the water forms were unchanged, and the bound water content was enhanced in the dewatered sludge. There is a study has reported on the direct gasification of dewatered sludge in SCW (Super Critical Water) and investigated the effects of water content on the SCWG (Super Critical Water Gasification) of dewatered sludge. It is reported that it is difficult to fully identify the influence of water content on direct gasification of dewatered sludge via SCW since the reason is not clear; like the whole chemistry of sludge gasification in SCW, how water content affect the reactions, etc. [13]. Furthermore, under the ideal conditions, it is possible to obtained high quality syngas production which has a good calorific value adjusting the feeding material combination. Because, if suitable sludge combination cannot be determined and fed to the reactor and also not be provided the optimum operation conditions (such as temperature, moisture, etc.), expected energy conversion cannot be obtained. So, one could state that the optimum targets of sewage sludge gasification is the production of a clean-combustible gas at high efficiency [14]. Compared to the conventional gasification process of wastes for electricity production, integrated gasification fuel cell systems seem to be preferable. An electrical efficiency of 30% can be thus effectively attained [15]. Researchers have investigated the hydrogen production potential from sewage sludge, by applying the downdraft gasification technique. In this case dewatering or drying prior to gasification neither is nor needed since wet sewage sludge provides the steam to the process. Sludge can be considered as one of the most promising gasification feedstocks for hydrogen production worldwide [16]. Syngas production during gasification process commonly used to produce electricity at mostly industrial scale. Judexet al. [17] analyzed two pilot plants based in Germany (Balingenand Mannheim) which were fueled by sewage sludge, and reported typical gas data for the mentioned plants. Each plant had produced gas with a calorific value of 765 kcal.m^{-3} and 1123 kcal.m^{-3} respectively. The authors reported that gasification was conducted successfully in fluidized bed and gas cleaning using granular bedfilter. Moltó et al. [18] investigated gasification and pyrolysis of physico-chemical (PC) and a biological (BIO) sludge. Ouadi et al. [19] investigated gasification of pre-conditioned rejects and de-inking sludge mixtures with wood chips in a fixed bed gasifier. The researchers obtained a gas with a composition of 16.24%H_2, 23.34% CO, 5.21% CH_4 and having a higher heating value (1744 kcal.(m3)$^{-1}$). They reported that paper mill rejects can be gasified in a fixed bed downdraft gasifier. Nipattummakul et al. [20] reported that, following fuel reforming with steam gasification, wastewater sludge can be a good source of fuel.

So, the aim of this study is to determine the best proper feeding combinations for a down draft fludised bed gasification pilot scale reactor processing hazardous/non-hazardous industrial sludges taken from dewatering unit of wastewater treatment plants of textile, dairy, vegetable and non-vegetable oil, glass and metal industries located in Thrace Region of Turkey. Moisture, ash and heating value contents were determined for sludge samples, char and cyclone dust samples that occurred as a result of gasification process. Then energy yields of the determined each combinations were calculated and as a result, the effect of the combination on the energy efficiency were assessed.

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2. MATERIALS AND METHODS

2.1. Material

This study was carried out in the Tekirdag province of Thrace region where the industrilisation is intense with approximately 1284 industrial enterprises. In this context, industrial sewage sludges, occured from industries working in the field of Textile, Dairy, Vegetable and Non-vegetable oil, Galss and Metal sectors in Çorlu-Çerkezköy- Muratlı and Malkara districts, were used as a main material. Experimental studies were run at a pilot scale downdraft gasification reactor, which have 1 ton.h^{-1} gasification capacity and established in the gasification plant located in İstanbul - Kemerburgaz. The schematic view is illustrated in Figure 1.

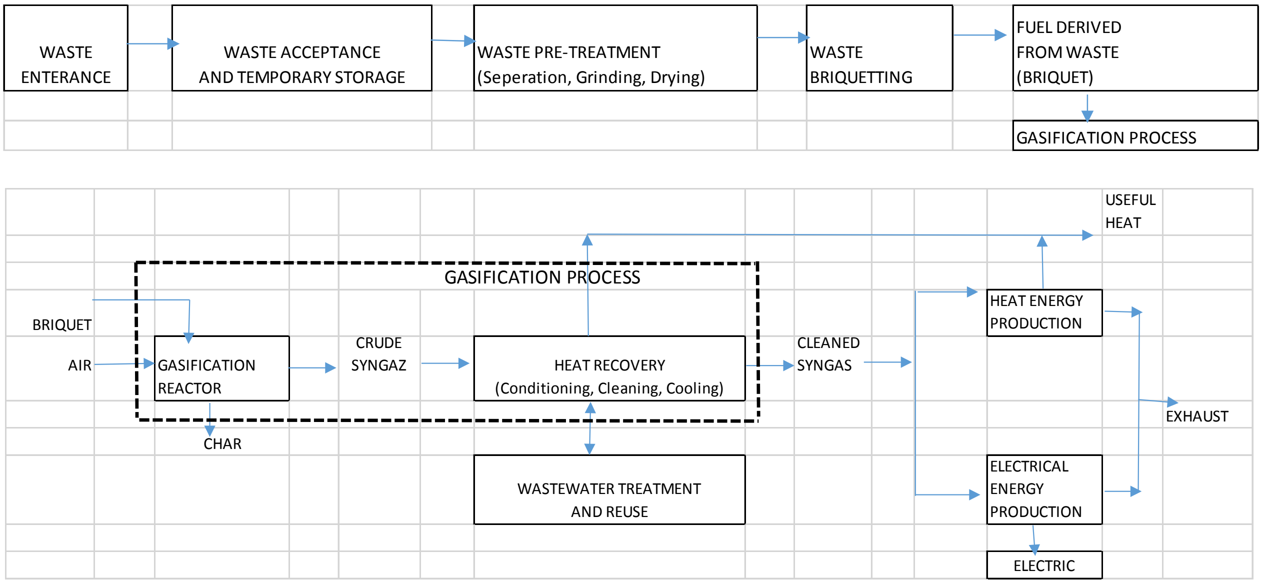


Figure 1. A schematic view of gasification plant worked in this study.

2.2. Method

2.2.1. Characterisation of the sewage sludge samples

In this study; gasification efficiency of hazardous-nonhazardous industrial sewage sludge consisting of different combination were evaluated on the base of both quantity and quality characterisation of char and cyclone dust occured as a solid waste during the gasification reactions . Samples were collected from three different wastewater treatment plant dewatering units working at every sectors mentioned above and then homogenized by grinding. Heating value, moisture and ash anlaysis were done according to the ASTM (American Society for Testing and Materials) standards in the context of characterisation studies. Determination of moisture, ash and heating value were done according to the ASTM D-3173 [21], TS EN 932-1 (ASTM D3174 - 04(2010)) [22] and ASTM D 5468-95 [23], respectively.

2.2.2. Determination of the sewage sludge combination

The reason for the determination of waste combination for gasification system is to enhance the heating value of waste having both low heating value and also high ash content before feeding to the reactor to obtain high energy. Ash content and calorific value are among the most important parameters showing the efficiency of the gasification system. If waste fed to the gasification reactor contains high organic and less inorganic material, the residue as ash content formed after the

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reactions will be less. So, practically, for high energy recovery, it is targeted that to obtain less ash but high syngas production. From this point of view, the feeding sludge combination were decided considering the ash content and heating value of industrial sewage sludges for the maximum energy that can be obtained. According to this approach and pre-study results, 4 different sludge combination were described as follows;

1) First combination: sewage sludges having high heating value,
2) Second combination: sewage sludges having low heating value and high ash content to identify the lowest gasification efficiency,
3) Third combination: sewage sludges having average heating value to identify the average energy efficiency,
4) Fourth combination: the mixture of all sewage sludges occurred from 5 different sectors without considering the heating value and ash content,

2.2.3. Measurement of char and cyclone dust

Char waste, occurred from the gasification of different sewage sludge combination fed to the reactor, was taken from under the gasification reactor after standing to cool it. Cyclone dusts captured in cyclone filters where through passed the syngas were also taken from the outlet of filter. 500 gr samples were collected in a small standard nylon bag and analysed without pretreatment for characterisation on the base of ash content and heating value. These values were used for calculation of energy efficiency and then examined sewage sludge combination were evaluated in terms of gasification efficiency.

2.2.4. Energy efficiency calculation of gasification reactor

The approximate efficiency of gasification reactor can be calculated from using pre-determined heating values char and cyclone dusts and considering the energy balance for gasification reactors as follows [24];

$$W_{Waste} * H_{Waste} = W_{Char} * H_{Char} + W_{Cyclone\ dust} * H_{Cyclone\ dust} + H_{Crude\ Syngas}$$

W_{Waste} = The amount of waste per hour (kg)
H_{Waste} = Heating value of waste fed to the reactor (kcal/kg)
W_{Char} = The amount of Char taken per hour (kg)
H_{Char} = Heating value of char (kcal/kg)
$W_{Cyclone\ dust}$ = The amount of cyclone dust per hour (kg)
$H_{Cyclone\ dust}$ = Heating value of char (kcal/kg)
$H_{Crude\ syngas}$ = Heating value of crude syngas (kcal/kg)

Furthermore, energy recovery efficiency (ή) was calculated by the following equation [25];

Energy Efficiency (ή) (%)= [(Heating value of produced crude syngas)/ (Energy inlet of gasification reactor)]*100

3. RESULTS AND DISCUSSION

3.1. Sectoral based characterization results of sewage sludges

Table 1 shows the typical characteristics of the sewage sludge samples taken from wastewater treatment plant dewatering units of textile, dairy, vegetable and non-vegetable oil, glass and metal industries researched in this study. By the way, moisture, ash content and heating values (before and after drying operation) of sewage sludge samples used to prepare sewage sludge combinations are summarized at Table 2. When these results are assessed in terms of gasification efficiency, it shown that except metal and glass industries, the other sludge samples were found suitable for gasification process in terms of both organic and inorganic contents by alone or mixture. On the

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other hand, it seems to be that, if convenient mixture can be prepared, it is possible to gasify these all sludges with together after a suitable stabilization or drying operation. According to Table 1, before drying, although the highest average moisture value was measured approximately as 64% for dairy industry, the lowest value was measured as 48% for metal industry. On the other hand, after drying, it was observed that all sludge samples had an average moisture values close to each. Furthermore, as expected, since the origin of metal and glass sewage sludges samples were chemical and inorganic, it was observed that they had high ash content (average 38% and 25% for metal and glass, respectively) and low heating value (average 1447 $kcal.kg^{-1}$=6 $MJ.kg^{-1}$ for metal and 1316 $kcal.kg^{-1}$= 5,5 $MJ.kg^{-1}$ for glass). On the contrary of this situation, it was identified that the vegetable and non-vegetable oil industrial sewage sludge had approximately two times higher heating value (average 11622 $kcal.kg^{-1}$= 48 $MJ.kg^{-1}$ for oil and average 5163 $kcal.kg^{-1}$= 21,6 $MJ.kg^{-1}$ for dairy) and nearly the same ash content (average 9,3% for oil and 9,5% for dairy) compared to dairy industrial sewage sludge.

Table 1. Typical characteristics of the sewage sludge samples taken from different industries

ANALYSIS	TEXTILE			VEGETABLE/NON-VEGETABLE OIL			DAIRY			METAL			GLASS		
	TEXTILE-1	TEXTILE-2	TEXTILE-3	VEGETABLE/ NON-VEGETABLE OIL-1	VEGETABLE/ NON-VEGETABLE OIL-2	VEGETABLE/ NON-VEGETABLE OIL-3	DAIRY-1	DAIRY-2	DAIRY-3	METAL-1	METAL-2	METAL-3	GIASS-1	GIASS-2	GIASS-3
ELUATE ANALYSIS															
Arsenic (As $mg.l^{-1}$)	<0,05	0,0009	0,002	0,015	0,037	<0,05	<0,0005	<0,0005	<0,0005	<0,01	<0,0005	<0,01	<0,0005	<0,0005	<0,0005
Barium (Ba $mg.l^{-1}$)	0,37	0,01	<0,002	0,063	0,054	<2	0,007	0,008	0,005	0,71	0,06	0,1	0,0017	0,0021	0,0032
Kadminyum (Cd $mg.l^{-1}$)	<0,05	<0,0005	<0,003	<0,0006	<0,0006	0,015	<0,0005	<0,0005	<0,0005	<0,001	<0,0005	0,031	0,001	0,0023	0,0019
Chromium (T-Cr $mg.l^{-1}$)	<0,05	0,004	0,34	<0,002	<0,002	0,053	<0,001	<0,001	<0,001	0,017	<0,001	0,144	0,029	0,036	0,041
Copper (Cu $mg.l^{-1}$)	<0,05	<0,01	<0,01	0,832	0,04	<0,2	<0,01	<0,01	<0,01	0,003	<0,01	11,2	<0,01	<0,01	<0,01
Mercury(Hg $mg.l^{-1}$)	<0,02	<0,0002	<0,0005	0,003	0,008	<0,001	<0,0002	<0,0002	<0,0002	<0,0001	<0,0002	<0,0008	<0,0002	<0,0002	<0,0009
Molybdenum (Mo $mg.l^{-1}$)	<0,05	0,002	<0,001	0,005	0,018	<0,05	0,023	0,016	0,019	<0,007	<0,001	<0,007	<0,001	<0,001	<0,001
Nickel (Ni $mg.l^{-1}$)	<0,05	<0,001	0,99	0,015	0,296	0,081	0,002	0,004	0,001	<0,003	0,002	9,1	0,004	0,004	0,036
Lead (Pb $mg.l^{-1}$)	<0,05	<0,0005	<0,001	<0,01	<0,01	<0,05	0,037	0,049	0,031	<0,015	<0,0005	5,6	0,0016	0,0016	0,0023
Antimony (Sb $mg.l^{-1}$)	0,068	<0,005	<0,003	<0,002	<0,002	<0,01	<0,005	<0,005	<0,005	<0,006	<0,005	0,022	0,014	0,014	0,019
Selenium (Se $mg.l^{-1}$)	<0,05	<0,001	<0,002	<0,002	<0,002	<0,01	<0,001	<0,001	<0,001	<0,01	<0,001	<0,01	<0,001	<0,001	<0,001
Zinc(Zn $mg.l^{-1}$)	0,177	<0,015	1,6	0,107	0,063	45	0,09	0,12	0,23	<0,001	0,016	55	0,065	0,065	0,098
Chloride (Cl- $mg.l^{-1}$)	14	107,2	122	35,4	479,3	349	61	39	69	201	65	2485	19	24	21
Floride(F- $mg.l^{-1}$)	0,475	1,1	2,9	<0,1	1,27	6,35	0,92	0,19	0,34	1,2	0,9	0,53	1,7	2,1	2,1
Sulfate(SO_4^{-2} $mg.l^{-1}$)	111	437,5	11	458,8	263	184	46	57	35	12	851	1119	37	56	44
Dissolved Organic Carbon (DOC, $mg.l^{-1}$)	119	311	713	828	946	980	908	756	812	6	38	15	51	42	28,4
Total Dissolved Solid (TDS, $mg.l^{-1}$)	954	3075	9342	1096	960	686	4116	2457	2369	662	1508	6318	195	211	181
Phenol index ($mg.l^{-1}$)	0,226	<0,02	0,14	<0,002	<0,002	15	<0,03	<0,03	<0,03	0,054	0,04	0,07	<0,03	<0,03	<0,03
ORİGİNAL WASTE ANALYSIS															
Total Organic Carbon (%)	6,1	4,8	10,6	19,7	24,8	21,2	18,8	14,5	16,9	2,7	1,6	0,9	3,6	3,1	2,1
BTEX (benzen, toluen, etilbenzen ve xylenes) ($mg.kg^{-1}$)	<0,25	<0,1	<0,003	<2	<2	<0,25	<0,25	<0,25	<0,25	0,062	<0,25	<0,02	<0,25	<0,25	<0,25
PCBs (Total) (mg/kg)	<0,1	<0,1	<0,003	-	3,2	<0,1	<0,1	<0,1	<0,1	<0,003	<0,1	<0,03	<0,1	<0,1	<0,1
Mineral Oil (C10-C40) ($mg.kg^{-1}$)	1102	681	777	1356,9	1371,5	49521	835	920	1017	<95	<100	<95	670	548	549
LOI (%)	98	94	97	87	91	95	85	89	94	58	43	64	57	68	62
pH	7,04	-	-	-	-	4,05	8,6	8,9	8,5	8,93	6,64	2,96	9,81	8,17	8,67
Moisture (%)	60,3	57,3	69	61	69	54	53	78	75	47	32	57	58,2	47	45,8

Table 2. Moisture, ash and heating values of sewage sludge samples

	BEFORE DRYING	AFTER DRYING		
INDUSTRY	**Moisture (%)**	**Moisture (%)**	**Ash (%)**	**High Heating Value (HHV) ($kcal.kg^{-1}$)**
Textile	54,3	14,8	1,5	3094
Biological wastewater treatment sludge	51,6	13,9	1,4	2946
(Activated sludge)	65,8	15,9	2,4	3999
Vegetable and Non-Vegetable oil	58	16,1	11,2	11631
Biological wastewater treatment sludge	67,4	17,2	9,7	13028
(Activated sludge)	50,4	15,8	7	10209
Metal	45,4	15,4	38	2084
Chemical wastewater treatment sludge	37	15,1	45,2	1455
	62,8	18,1	30,3	802
Dairy	44,3	15,3	13,6	7820
Biological wastewater treatment sludge	75,8	18,9	10,3	3303
(Activated sludge)	73,2	19,1	4,7	4366
Glass	64,2	17,6	34,3	1656
Chemical wastewater treatment sludge	51,4	14,8	21	1492
	52,6	14,1	19,2	802

1 kcal=4,184 KJ, 1 MJ= 1000 kJ

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Since there are no any literature related with this type of characterization determined for different industrial sewage sludge gasification, these values found in this study were the original. But, when these results were compared the results studied for miscellaneous sewage sludges in the literature, these values are meaningful according to the sludge origin and in terms of the magnitude of values [16, 26 , 27, 28, 29].

3.2. Characterization results of sewage sludges combinations fed to the gasification reactor

Moisture, ash and heating value of sewage sludge combinations fed to the gasification reactor are given at Table 3. When these results are evaluated, moisture values of waste combinations fed to the reactor were found close to each other and suitable for the gasification process. Furthermore, while the highest heating value and the lowest ash content were measured at Combination 1, the lowest heating value and the highest ash content were measured for Combination 2, as expected. By the way, it was observed that considered Combination 3 and Combination 4 results showed the similiar character in terms of considered parameters. Consequently, low ash content was observed at sludge combination which has high heating value. But, because of the heterogeneous character of some combinations (Combination 3 and Combination 4), were studied, high ash content was observed at moderate heating value compared to Combination 2. Furthermore, heating values of feeding combinations were found consistent with those reported in the literature [24].

Table 3. Characterization of sewage sludge combinations fed to the gasification reactor

Sludge Combination fed to the reactor	**Mositure (% w/w)**	**Ash (% ww/ww)**	**HHV (kcal.kg^{-1})**
Combination 1 **(Textile 3+ Vegetable and Non-vegetable oil 2+Dairy 1**	16,5	8,9	8170
Combination 2 **(Textile 2+ Metal 1+Glass 2)**	14,9	22	2080
Combination 3 **(Textile 1+ Metal 2+ Glass 1+ Dairy 2 + Vegetable and Non-vegetable oil 1)**	17	23	4120
Combination 4 **(Textile all+ Vegetable and Non-vegetable oil all+ Metal all + Dairy all + Glass all)**	16,5	17,6	4510

3.3. Characterization results of char wastes and cyclone dust

Determined sewage sludge combinations were fed to the downdraft gasification reactor and then occurred char waste under the reactor and cyclone dust taken from the outlet of cyclone filter were analysed to determine heating value and ash content. Measured values are summarized at Table 4. Cyclone dusts are the waste dust entrained by the crude syngas gas from the gasification reactor. It is expected that these dusts have minimum heating value. But, during the process, it is possible to see an occured dust form waste which does not undergo any thermal decomposition and entrained by the crude syngas to the outlet. According to the Table 4, ash content of char waste and cyclone dust occurred from all combinations were found around 80-90%. On the other hand, when the heating values were assessed, it is observed that the heating values for char waste are found in the range of 2300-3500 kcal.kg^{-1} for all combination except Combination 2. The reason of it can be the dominant inorganic character of this combination because of intensive metal and glass sewage sludge content. Elif [24] found the heating values of char and cyclone dust samples 1500-2500

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kcal.kg^{-1} and 600-1200 kcal.kg^{-1} for industrial waste having 3500-5500 kcal.kg^{-1} heating value in a downdraft gasification reactor. So, results obtained in this study were found compatible with the literature too. Furthermore, the highest ash content and heating value were obtained for char waste at the gasification of Combination 1. On the other hand, when ash content and heating value of cyclone dust occurred from all combination are assessed, while the highest ash content determined for cyclone dust was obtained at Combination 3, the highest (but three times lower than char waste) heating value was obtained at Combination 1. This results show that there are no any waste in dust form that not undergo any thermal decomposition during the gasification reactions since the heating value of samples were low and ash contents were high. But on the contrary this, char waste characteristics show that it can be reprocessed in gasification or any thermal process before disposal to landfill since it has still a valuable calorific value as well as sewage sludge.

3.4. Gasification efficiency

Efficiency of gasification reactor is expressed as the amount of recovered syngas from the waste fed to the reactor as an energy input. In this study, as reported in the literature [24], gasification reactor efficacy was calculated considering the energy balance for gasification reactors. In this calculation, heating values of char and cyclone dusts determined in this study were used and supposed that all energy outputs except char and cyclone dust were found in syngas. Gasification efficiency of sewage sludge combinations fed to the reactor were given at Table 5. Averagely, 1 000 m^3 crude syngas production per hour was assumed at his calculation.

Table 4. Characterization results of char wastes and cyclone dust

		CHAR WASTE			CYCLONE DUST		
Sludge Combination fed to the reactor	**Sludge amount fed to the reactor (kg.day^{-1})**	**Char amount under the reactor (kg.day^{-1})**	**Ash (% ww/ww)**	**HHV (kg.kg^{-1})**	**Cyclone dust amount (kg.day^{-1})**	**Ash (% ww/ww)**	**HHV (kg.kg^{-1})**
Combination 1 **(Textile 3+ Vegetable and Non-vegetable oil 2+Dairy 1**	7 000	500	88	3509	20	75	1107
Combination 2 **(Textile 2+ Metal 1+Glass 2)**	6 780	500	76	834	20	73	1017
Combination 3 **(Textile 1+ Metal 2+ Glass 1+ Dairy 2 + Vegetable and Non-vegetable oil 1)**	5 200	420	73	2486	20	88	610
Combination 4 **(Textile all+ Vegetable and Non-vegetable oil all+ Metal all + Dairy all + Glass all)**	5 850	475	78	2373	20	82	884

Table 5. Gasification efficiency of sewage sludge combinations fed to the reactor

Sludge Combination fed to the reactor	**Input energy (kcal)**	**Heating value of Output Char (kcal)**	**Heating value of ouput cyclone dust (kcal)**	**Heating value of output crude syngas (kcal)**	**Output crude syngas (kcal.(m^3)$^{-1}$)**	**Efficiency (%)**
Combination 1	2.382.916,67	73.100	922,50	2.308.894,17	2.308,9	**97**
Combination 2	587.600,00	17.370,83	847,50	1.384.798	1.384,8	**94**
Combination 3	892.666,67	43.496,25	508,30	918.888,2	918,88	**95**
Combination 4	1.099.312,5	46.965,63	736,42	1.152.062	1.152,06	**96**

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It is aimed from the gasification process to separate the organic components, found in the waste, with crude syngas in a minimum loss. But, although the quality of obtained syngas is not equal to the natural gas, since it has a specific heating value, it will provide more advantage in terms of efficiency. At normal condition, the heating value of syngas is expected between 1000-2600 kcal.$(m^3)^{-1}$ [30]. So, generally it is accepted that the reactors are very efficient at the conditions provided both over 1000 kcal.$(m^3)^{-1}$ heating value and lowest energy losses in terms of char and cyclone dust. From this point of view, Table 5 shows that gasification efficiency of sewage sludge combinations fed to the reactor ranged between 94-97 %. While the highest energy efficiency was obtained at Combination 1, the lowest efficiency was observed at Combination 2 as expected. But, when the magnitude of them was assessed, it can be said that there is no a significant difference between them.

4. CONCLUSIONS

This research indicates that; sectoral based characterization results of sewage sludges researched in this study showed that all sludges can be determined as hazardous except metal and glass in terms of landfill criteria accepted in both EU and Turkey legislation. The heating values of sewage sludges samples researched in this study were measured between 800-13.000 kcal.kg^{-1}. Sewage sludges combinations determined in this study showed a suitable character for the gasification process in terms of both moisture, ash content and heating value. Ash content of char waste and cyclone dust occurred from all combinations were found around 80-90%. Heating values for char waste are found in the range of 2300-3500 kcal.kg^{-1} for all combination except Combination 2. The reason of it can be the dominant inorganic character of this combination because of intensive metal and glass sewage sludge content. Char waste characteristics show that it can be reprocessed in gasification or any thermal process before disposal to landfill since it has still a valuable calorific value as well as dried raw sewage sludge. Gasification efficiency of sewage sludge combinations fed to the reactor ranged between 94-97%. So, results obtained in this study were found compatible with the literature too. Furthermore, it is observed that sludge combination, which has high calorific value and low ash ratio, had the highest energy efficiency compared to the other sludge combinations. So, it is consider that both hazardous and non- hazardous treatment sludges occurred from miscellaneous industries located in this region, if the proper sludge combination can be prepared, gasification process can be the best industrial sludge management method for this region both industrial sludge minimisation and energy recovery before landfill.

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References

[1] Verkooijen AHM., 1987. Combustion of sewage sludge with heat recovery. *Resources and Conversation*, **14**, 257-272.
[2] Stone RJ, Ekwue EI, Clarke RO. 1998. Engineering properties of sewage sludge in Trinidad. *J Agric Engng Res*, **70**, 221-230.
[3] Littlewood K.1977. Gasification: theory and application. *Prog Energy Combust Sci.* , **3**, 35-71.
[4] Bridgwater AV. 1995. The technical and economic feasibility of biomass gasification for power generation. *Fuel*, **74(5)**, 631-653.
[5] Chun, Y.N.; Ji, D.W.; Yoshikawa, K. 2013. Pyrolysis and gasification characterization of sewage sludge for high quality gas and char production. *J. Mech. Sci. Technol.*, **27**, 263–272.
[6] Kang, S.W.; Dong, J.I.; Kim, J.M.; Lee, W.C.; Hwang, W.G. 2011. Gasification and its emission characteristics for dried sewage sludge utilizing a fluidized bed gasifier. *J. Mater. Cycles Waste Manag.*, **13**, 180–185.

ISBN: 978-960-6865-94-7

[7] Werle, S.; Wilk, R.K. 2010. A review of methods for the thermal utilization of sewage sludge: The Polish perspective. *Renew. Energy*, **35**, 1914–1919.
[8] Werle, S. 2013. Sewage sludge gasification: Theoretical and experimental investigation. *Environ. Prot. Eng.*, **39**, 25–32.
[9] Nilsson, S.; Gómez-Barea, A.; Cano, D.F. 2012. Gasification reactivity of char from dried sewage sludge in a fluidized bed. *Fuel*, **92**, 346–353.
[10] Werle, S.; Dudziak, M. 2013. Gaseous Fuel Production from Granular Sewage Sludge via Air Gasification—Influence of the Waste Treatment Configuration on Sludge Properties and Producer Gas Parameters. *In Proceedings of the 8th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems*, September 22–27, Dubrovnik, Croatia, 1–10.
[11] Phuphuakrat, T.; Nipattummakul, N.; Namioka, T.; Kerdsuwan, S.; Yoshikawa, K. 2010. Characterization of tar content in the syngas produced in a downdraft type fixed bed gasification system from dried sewage sludge. *Fuel*, **89**, 2278–2284.
[12] Mahmoud A, Olivier J, Vaxelaire J, Hoadley AF. 2010. Electrical field: a historical review of its application and contributions in wastewater sludge dewatering. *Water Research*, **44**, 2381-2407.
[13] Xu Z.R., Zhu W., Li M. 2012. Influence of moisture content on the direct gasification of dewatered sludge via supercritical water, *International Journal of Hydrogen Energy*, **37**, 6527-6535.
[14] McAuley, B., Kunkel, J., Manahan S.E. 2001. A new process for drying and gasification of sewage sludge. *Water Engineering and Management*, **May**, 18– 23.
[15] Maniatis, K., 1999. Overview of EU thermal gasification projects. In: Sipila, K., Korhonen, M., (Eds.), Power production from biomass III, gasification & pyrolysis R&D for industry (192), VTT Symposium, VTT Espoo.
[16] Dogru, M., Midilli, A. Howarth, C.R. 2002. Gasification of sewage sludge using a throated downdraft gasifier and uncertainity analysis. *Fuel Process Technology*, **75**, 55-82.
[17] Judex J.W., Gaiffi M., Burgbacher H.C. 2012. Gasification of dried sewage sludge: sta-tus of the demonstration and the pilot plant, *Waste Manage.* **32**, 719–723.
[18] J. Moltó, et al., 2012. Gas production during the pyrolysis and gasification of biologicaland physico-chemical sludges from oil refinery, *J. Anal. Appl. Pyrol.* http://dx.doi.org/10.1016/j.jaap.2012.09.012.
[19] Ouadi M., Brammer J.G., Kay M., Hornung A., 2013. Fixed bed downdraft gasificationof paper industry wastes, *Appl. Energy*, **103**, 692–699.
[20] Nipattummakul N., Ahmed I., Kerdsuwan S., Gupta A.K., 2010. High temperature steam gasification of wastewater sludge, *Appl. Energy*, **87**, 3729–3734.
[21] ASTM D-3173 standardı Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, The American Society for Testing and Materials, the United States of America.
[22] ASTM D3174 - 04(2010) Standard test Method for Ash in the Analysis Sample of Coal and Coke from Coal, The American Society for Testing and Materials, the United States of America.
[23] ASTM D 5468-95 Standard Test Method for Gross Calorific and Ash Value of Waste Materials, The American Society for Testing and Materials, the United States of America.
[24] Güzel E., 2011. Industrıal Waste Gasıficatıon And The Characterızatıon Of Solıd Effluents (Char, Cyclone Dust And Clınker) Of Gasıficatıon Process, M.Sci. Thesis, Istanbul Technical University, İstanbul.
[25] CRC Press, Rajvanshi, AK. In: Goswami DY, editör. 1986. Alternative energy in agriculture, **Vol.II.** , 83-102
[26] Dotti F. Ramey, Nicholas P.G. Lumley, Ana L. Prieto, Jason M. Porter, Tzahi Y. Cath, 2015, Evaluating air-blown gasification for energy recovery from wastewater solids: Impact of biological treatment and point of generation on energy recovery / Sustainable Energy Technologies and Assessments. *Sustainable Energy Technologies and Assessments*, **9**, 22–29.
[27] Cao Y., Wang Y., 2006. A novel biomass air gasification process for producing tar-free higher heating value fuel gas, *Fuel Process Technol*, **87**, 343–53.
[28] Skoulou V., Zabaniotou A., Stavropoulos G., Sakelaropoulos G., 2008. Syngas production from olive tree cuttings and olive kernels in a downdraft fixed-bed gasifier, *International Journal of Hydrogen Energy*, **33**, 1185-1194.
[29] Ongen, A., Kurtulus Ozcan H., Arayıcı S., 2013. An evaluation of tannery industry wastewater treatment sludgegasification by artificial neural network modeling, *Journal of Hazardous Materials*, **263**, 361– 366.
[30] http://www.eie.gov.tr/turkce/YEK/biyoenerji/04-gazlaştırma/gz_gelecek.html (accessed May 1st, 2011).

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Minimization of reservoir dredged material using its addition in concrete

J. Junak*, N. Junakova

Institute of Environmental Engineering, Faculty of Civil Engineering, Technical University of Kosice, Vysokoskolska 4, 042 00 Kosice, Slovak Republic.
*Corresponding author: Email: Jozef.Junak@tuke.sk

Abstract

Long-term and very serious world problem is solid waste production which also arises in water management through silting of reservoirs with sediments. After dredging sediments can be disposed, but managers try to find environmentally friendly solutions. Considering sediments perpetual availability, particle size and chemical composition, they are regarded as a suitable raw material in construction industry.

The objective of this research is to find new paths of management of the material dredged from the small reservoir Klusov (Slovakia). Focus is made on the possibility of a recycling method, which consists of the reuse of sediments as an alternative raw material in concrete production. Sediments are used as a partial substitute of natural aggregate (fraction 0/4 mm) and as a partial cement replacement in concrete. The effects of the sediment addition on the concrete technological properties (flexural strength and freeze-thaw resistance) are determined. Concrete specimens were pressed and cured for 28, 90 and 365 days and subjected to 50 cycles of freeze-thaw testing after 365 days.

The flexural strengths of concrete specimen prepared as a natural aggregate replacement were higher when compared with the reference mixture at all ages of hardening. Flexural strengths of the sample prepared as a cement replacement were slightly lower as the reference mixture and it was about 4.0 MPa after 90 days of curing. The results of the frost resistance coefficient and the weight loss after 50 cycles of freeze-thaw show that tested concrete specimens meet the standard requirements for frost resistant concrete class XF2.

Keywords: sediments; reuse; flexural strength; freeze-thaw resistance

1. INTRODUCTION

Most reservoirs in the world, from small through medium to large capacity, are subject to siltation problems to some degree. Sediments reduce the storage capacity of the world's reservoirs by more than 1 % per year and the useful lifetime of the reservoirs to only 22 years on average [1]. Therefore, accumulated sediment should be periodically removed in order to maintain the effectiveness of these structures [2]. However, the management of dredged sediments is a significant issue in the world. Several assessments demonstrated that the total amount of sediment dredged in Europe reaches 100-200 million cubic meters per year [3]. Water management organizations solves the problems with the managing of all dredged materials. These materials can be disposed, but managers try to find environmentally friendly solutions for dredged sediments [4,5]. With the shortage in some region of the world of natural resources in many engineering fields, the beneficial reuse of sediments can optimize the management of the natural resources. In this order, the valorization of dredged materials as a resource constitutes a technical and economical challenge [6]. Dredged material can constitute a new source of materials in building construction and it can be utilized as a minor or major component in construction industry [7-10].

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This study is focused on the possibilities of dredged sediments minimization by their reusing in concrete.

2. MATERIALS AND METHODS

2.1 Sediment characterization

Reservoir sediments were collected from the Klusov small water reservoir, situated in the agricultural watershed in Eastern Slovakia. The composite sediment samples were taken from the drained reservoir from two sites: near the dam due to deposition of the fine-grained particles smaller than 63 µm and at inflow to the reservoir because of sedimentation of coarse-grained particles. In laboratory conditions, the composite samples were air dried at room temperature, any coarse lumps were crushed and samples were homogenized.

Particle size distribution of sediment samples were conducted through a combination of dry sieve method and laser diffraction method. Coarse-grained sediment sample was analysed by passing the dry composite sediment sample through a standard series of sieves with mesh sizes from 4 mm to 0.125 mm. Undersize particles were analysed by laser diffractometry using a Mastersizer 2000 (Malvern Instruments, UK) with a Hydro 2000S wet dispersion unit. Fine-grained sediment sample was analysed using the same equipment. Measurement parameters were: pump speed - 2,800 rpm; ultrasonic - turned on for 5 min after sample addition.

Crystalline minerals present in the sediments were identified by X-ray diffraction (XRD) analysis with diffractometer Bruker D2 Phaser (Bruker AXS, GmbH, Germany) in Bragg-Brentano geometry (configuration Theta-2Theta), using the 1.54060 Å CuKα radiation, Ni Kβ filters and scintillation detector at a voltage of 30 kV and10 mA current. Scan conditions were: recording times about 2 h, a step size of 0.04° (2Θ) and step time of 3 s. The XRD patterns were processed using the software Diffrac. EVA v. 2.1. The ICDD PDF database (ICDD PDF – 2 Release 2009) was utilized for the phase identification.

The chemical composition of the sediments (oxide analysis) was determined by X-ray fluorescence method using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10,000 pulses.

2.2 Partial sediment addition in concrete

In this work, a case study is presented in order to find the solution to minimize reservoir sediments using their addition in the concrete production. The coarse-grained sediments were used as a partial substitute of natural aggregate (fraction 0/4 mm) and fine-grained sediments were used as a partial cement replacement in concrete production.

Portland cement (CEM I 42.5 N) and two different fractions of natural aggregate (0/4 mm and 4/8 mm) were used as other raw materials for preparing the concrete mixtures. Natural aggregate was evaluated according to the Slovakian standard STN EN 12 620 (2008).

The concrete specimen composition was designed according to STN EN 206-1 (2002) for strength class C 25/30. Water-to-cement ratio of 0.5 was used and no plasticizer was added.

Three concrete mixtures were prepared. Control concrete mixture (M0) was prepared by mixing cement (CEM I 42.5 N), natural aggregate (0/4 mm and 4/8 mm) and water at solid/liquid ratio of 0.5. The second mixture (M1) was prepared using 40:60 proportions of fine-grained sediment and Portland cement. To study the partial natural aggregate replacement by coarse-grained sediments in concrete (20 wt. % of 0/4 mm sediment fraction), another mixture (M2) was prepared.

Concrete specimens were hardened for 28, 90 and 365 days, than they were tested for flexural strengths using a strength testing machine ELE 2000 (ELE International Ltd, GB) and were loaded until failure. After 365 days of hardening, the resistance of the blended concrete specimens to freeze-thaw attack was verified by laboratory tests using CDF/CIF freeze-thaw tester (Schleibinger

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Geräte, Germany). The concrete samples were subjected to 50 cycles of freezing and thawing according to the procedure as described in the Slovak Standard STN EN 73 1322 [11]. Specimens were immersed completely in the freezing medium in a special container. In the freeze-thaw test, concrete specimens were cyclically frozen in range from 20 °C to -20 °C over the course of 12 h (1 cycle).

3. RESULTS AND DISCUSSION

The particle size distribution of sediments, characterized by grading curves, is presented in Figure 1. The results indicate that the clay/silt fraction dominate in fine-grained sediment sample, used as a partial cement replacement in concrete, with more than 95 % proportion of particle size below 0.063 mm. Coarse-grained sediment sample, used as a replacement of 0/4 fine aggregate fraction in concrete, contains about 50 % of sand and gravel particles.

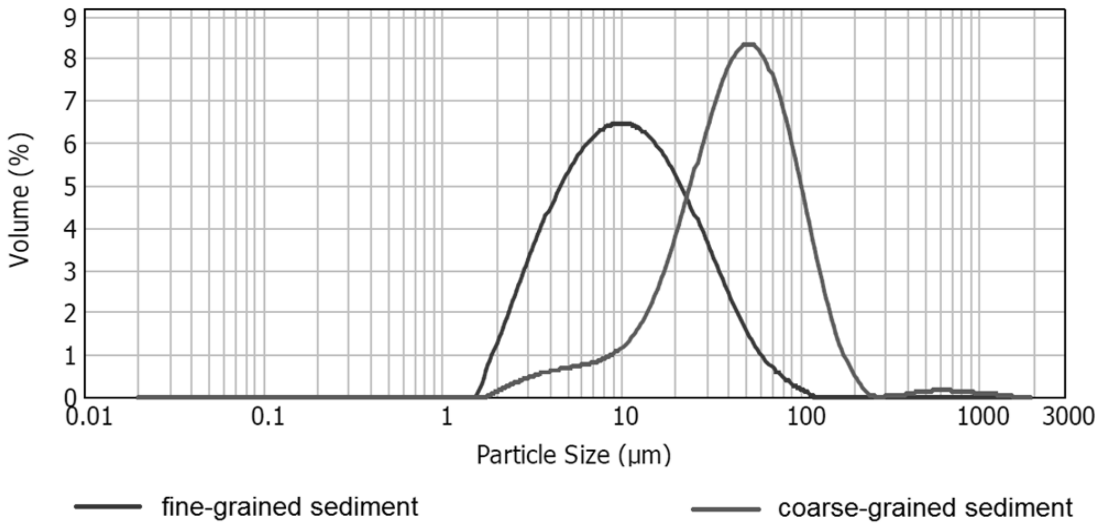


Figure 1. Particle size distribution measured for fine and coarse-grained sediments

The X-ray diffractogram of the sediments demonstrates that quartz peaks are dominant and remarkably visible, followed by muscovite peaks, what confirmed the presence of silicates.

The chemical composition of the sediments obtained from XRF analysis (Table 1) reveals that SiO_2 and Al_2O_3 predominantly compose the sediment samples. Toxic compounds were not recorded in investigated sediments. Other main ingredients of fine-grained sediment are Fe_2O_3, K_2O, MgO and CaO that are important in Portland cement manufacture.

In order to find out the feasibility of manufactured blended concrete mixtures using the sediments, a total of three concrete mixtures were subjected to flexural strength after 28, 90 and 365 days of hardening and 50 cycles of freezing and thawing after 365 days of curing. The results of this testing are given in Table 2. The value of flexural strength is the average of three concrete prisms for each mixture at testing age. Figure 2 illustrates the flexural strengths development after 28, 90 and 365 days of curing.

To evaluate the frost resistance of concrete mixtures, coefficient of the frost resistance and weight loss were determined. According to STN EN 73 1322 if the coefficient of the frost resistance is higher than 0.85 for given number of cycles and the weight loss during testing is less than 5 %, concrete is considered as frost resistant.

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Table 1. Chemical composition of the sediments

wt.%	fine-grained sediment	coarse-grained sediment
SiO_2	68.56	49.66
Al_2O_3	18.01	5.39
Fe_2O_3	5.15	1.51
MgO	2.40	1.06
K_2O	2.95	0.68
CaO	1.10	0.57
TiO_2	1.12	0.20
MnO	0.09	0.03
P_2O_5	0.26	0.11
SO_3	0.11	0.05
Cl	0.03	0.01

Table 2. The flexural strengths of composites after 28, 90 365 days of curing and the coefficient of the frost resistance C_f and the weight loss ΔW_n after 50 cycles of freeze-thaw testing

	Mix number	M0-control	M1	M2
Flexural strength (MPa)	28 days	4.93	4.45	5.41
	90 days	4.95	4.51	5.88
	365 days	4.43	4.08	6.59
Freeze-thaw testing after 365 days	C_f	1.03	0.85	0.86
	ΔW_n (%)	1.62	2.50	1.33

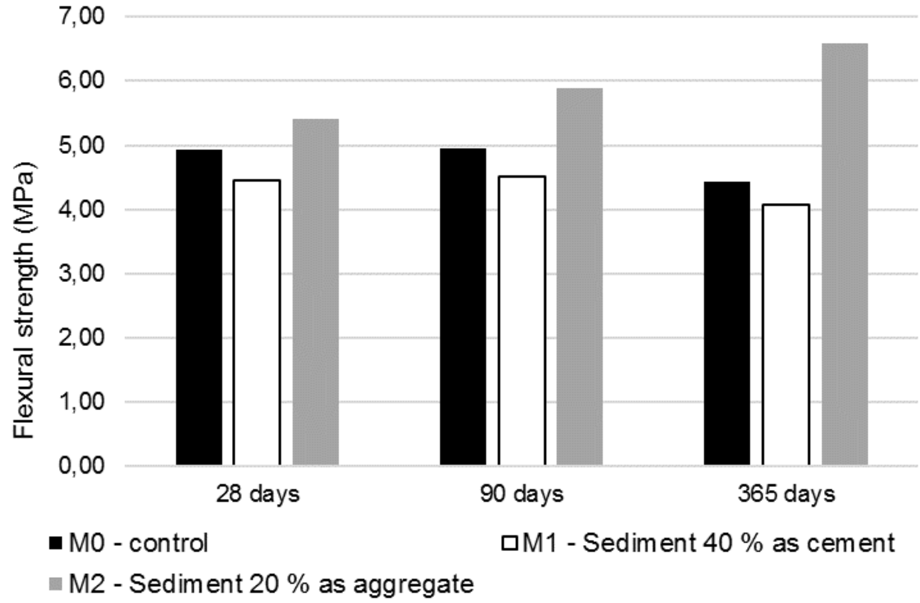


Figure 2. The flexural strength development of concrete specimens

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The development of flexural strengths in the sample M1 (Figure 2), wherein the sediment was used as a 40 percent cement replacement, followed the trend of flexural strength achieved in the control sample. However, the observed flexural strengths were lower and reached the strengths in the range of 4.08 - 4.51 MPa. The first 90 days of curing, the strength increased, after a year the samples expressed lower strengths.

The opposite progress occurred in the sample M2, where sediment was used as a 20% aggregate replacement. With increasing curing time, the strengths were increased, and after a year, mixture was reaching values at 6.59 MPa.

Results after 50 freeze-thaw cycles indicate, that tested concrete specimens have reached the values of the frost resistance coefficient equal or higher than 0.85, even control concrete composite M0 obtained this value of 1.03. This may mean that the process of concrete hydration continued during the freeze-thaw test. The weight loss values after 50 cycles of freeze-thaw testing were in range from 1.33 % (mixture composed of the 20 wt. % of 0/4 natural aggregate replacement by coarse-grained sediments in concrete) to 2.5 % in mixture prepared at a 40:60 fine-grained sediment/cement weight ratio. We can state, that the standard's requirement of maximum 5 % weight loss was satisfied. The results of the frost resistance coefficient and the weight loss after 50 cycles of freeze-thaw show that tested concrete specimens meet the standard requirements for frost resistant concrete class XF2.

4. CONCLUSIONS

This work presents a case study in order to find the solution to minimize reservoir sediments dredged from the Klusov small water (Slovakia) by their addition in the concrete. Sediments were used as a partial substitute of natural aggregate (fraction 0/4 mm) and as a partial cement replacement in concrete. The flexural strength results showed that specimens containing fine-grained sediment as a 40 % cement replacement achieved the values 8 % lower compared to control mixture after 365 days of hardening. The flexural strength results reveals that the substitution of natural aggregate by the coarse-grain sediment in the concrete is feasible and reach the values 49 % higher comparing to control mixture after 365 days of curing. In this case, longer curing time had a positive impact on the flexural strength. The results of the frost resistance coefficient and the weight loss after 50 cycles of freeze-thaw show that tested concrete specimens meet the standard requirements for frost resistant concrete class XF2. For wider use of fine-grained sediment in concrete production, the dredged material mineralogy need to be modified by ingredients improving its pozzolanic properties.

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References

[1] Batuca, D. G., Jordaan, J. M., 2000. *Silting and desilting of reservoirs*. Edit. A.A. Balkema, Rotterdam.

[2] Sumi, T., Hirose, T., 2009. Accumulation of sediment in reservoirs. *Water Storage, Transport, and Distribution. Encyclopedia of life support systems* (ed Y. Takahasi), UNESCO, UK

[3] LIFE+ Environment Policy and Governance, 2012. After-LIFE communication plan. Report. *SEDI.PORT.SIL - Recovery of dredged SEDIments of the PORT of Ravenna and SILicon extraction.* http://ec.europa.eu/environment /life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=LIFE09_ENV_IT_000158_AfterLIFE.pdf (accessed March 20, 2016).

[4] Crawford, A., 2004. *Beneficial reuse of Baltimore dredged sediments as vertical cutoff wall backfill material*. Master degree Thesis. University of Maryland, Maryland, USA

[5] Deibel, I., Lampe, C., Ulbricht, J.P., Cnudde, T., Dessel, G., 2007. Beneficial Use. *Sustainable Management of Sediment Resources*, **2**, 119–132.

[6] International Association of Dredging Companies – IADC, 2009. Facts about dredged material as a resource. https://www.iadc-dredging.com/ul/cms/fck-uploaded/documents/PDF%20Facts%20About/facts-about-dredged-material-as-a-resource.pdf (accessed March 20, 2016).
[7] Mezencevova, A., Yeboah, N.N., Burns, S.E, Kahn, L.F., Kurtis, K.E., 2012. Utilization of Savannah harbor river sediment as the primary raw material in production of fired brick. *Journal of Environmental Management*, **113**, 128-138
[8] Chen, H.J., Yang, M.D., Tang, C.W., Wang, S.Y., 2012. Producing synthetic lightweight aggregates from reservoir sediments. *Construction and Building Material,* **28**, 387-394.
[9] Romero, M., Andrés, A., Alonso, R., Viguri, J., Rincón, J.M., 2009. Valorisation of contaminated marine sediments to produce ceramic construction materials. *Spanish National Conference on Advances in Materials Recycling and Eco – Energy*, 45-48.
[10] Mensinger, M.C., 2008. *Cement-lock® technology for decontaminating dredged estuarine sediments.* Topical report on beneficial use of ecomelt from Passaic river sediment at Montclair State University, New Jersey. Des Plaines, Illinois: Gas Technology Institute, USA
[11] STN EN 73 1322, 1968. Determination of frost resistance of concrete.

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Remediation of Contaminated Media

PROTECTION AND RESTORATION OF THE ENVIRONMENT XIII

Variation of the As(V) lability on mine-impacted soils as a function of stabilization period, amending dose/timing, and soil properties

M. Kim[1], J. Kim[1], Y. S. Kim[1], S. Hyun[1*], D. H. Moon[2]

[1] Division of Environmental Science and Ecological Engineering, Korea University Seoul, 02841 Korea.
[2] Department of Environmental Engineering, Chosun University Gwangju, 61452, Korea.
* Corresponding author: Email: soilhyun@korea.ac.kr

Abstract

The lability of As(V) in amended mine soils was investigated as functions of incubation period, amendment dose, and application timing. Mine soils contaminated with 26-209 mg kg^{-1} of As(V) were treated with two amending materials (mine discharge sludge (MS) and steel-making slag (SS)) and were incubated for a 6-month period. After each designated time, As(V) was fractionized by five sequential extraction steps (F1-F5). Over the 6-month period, the fraction of As(V) was characterized by a reduction (26.9-70.4%) of the two labile fractions (F1 and F2) and a subsequent increase (7.4-29.9%) of F3 (r^2=0.956). Two recalcitrant fractions (F4 and F5) remained unchanged. Temporal change of As(V) lability was well described by two-domain model (kfast, kslow, and Ffast). The immobilization (%) was well correlated with the fast-immobilization domain (Ffast, r^2=0.806), but poorly with the kinetic rate constants (kfast and kslow). As expected, the initial 2.5%-MS addition resulted in lower efficacy than the initial 5% addition, but second 2.5%-MS addition after the lapse of 3-month led to a dramatic (>30%) decrease of labile As(V). The As(V) immobilization (%) by iron-rich materials is essentially governed by the presence of clay, Fe-oxides, kinetically labile As(V) in contaminated soils. However, the mass ratio of labile As(V) /amendment and the timing of amendment addition should also be considered to enhance the stabilization efficacy.

Keywords: immobilization; labile fraction; abandoned mine soils; As(V)

1. INTRODUCTION

Immobilization techniques have been successfully used for many metallic element remediation site, in which amendments are applied to reduce chemical lability of metallic elements in contaminated soils. In most previous studies, the amendment efficacy was determined by measuring the reduced mass of labile fraction after a single designated incubation time. The stabilization efficacy is varied with amendment application rates since stoichiometric ratio between labile form and amending materials is essentially different. In addition, the incubation period required to attain steady state stabilization varies with amendment dose. Although it is apparent that the amending methods (amendment dose, timing, and aging period) can affect the stabilization efficacy, the change of labile fraction under different amending conditions has not been well understood. Therefore, the objectives of this study were to collect As(V) fractionation data from Fe oxide-rich material treated mine soils as a function of ageing period and to evaluate soil factors that determine the kinetic rate and efficiency of As(V) immobilization. The effects of amendment dose and addition timing were also investigated.

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2. MATERIALS AND METHODS

Six subsurface soils (S1, S2, S3, M1, M2, and M3; three soils from S and M mines, respectively) were obtained from two abandoned mine sites. Two industrial byproducts, coal mine discharge sludge (MS) and steel making furnace slag (SS), were used for iron-rich amendments.

Five g of amendments (MS and SS) was added to 100 g of the six mine soils (S1, S2, S3, M1, M2, and M3). The amended samples were incubated at 25 ± 2^{o}C over 6-month. All sample pots were triplicates. For S2 and M2 soils, the effect of amendment dose and timing on the immobilization of As(V) was further assessed. Total 5 g of MS addition was split into two discrete times. The first 2.5 g was added at the beginning then the second 2.5 g was added after the lapse of 3-month. The sequential extraction procedure proposed by Wenzel et al. (2001) was used for As(V) fractionation.

3. RESULTS AND DISCUSSION

3.1. Characterization of As-contaminated mine soils and the amendments

As(V) concentration of the six mine soils highly exceeded the regulatory level (i.e., 25 mg kg^{-1}) in Korea. The fractionation results showed that the quantities of the five fractions were in the order of F3 > F4 ≥ F2 ≅ F5 >> F1. The pH values of the MS and SS were slightly alkaline (pH > 8) due to the lime material addition during their formation.

3.2. Fractional change of As(V) in the amended samples

A reduction of the two labile fractions (F1 and F2) was apparent, whereas F3 fraction increased slightly. Note that the most abundant As(V) fraction over the 6-month was consistently the F3, which accounted for 36–54.8% of total As(V) mass. In contrast, the change of As(V) mass in both the crystalline oxide bound (F4) and the residual fraction (F5) was insignificant ($p < 0.01$) under the conditions of this study.

The proportion of the nonspecifically adsorbed fraction (F1) decreased markedly in all amended samples within the first 2 months followed by a slower decrease with incubation time, indicating a biphasic decay pattern. 33–80% of initial F1 and 26–70% of initial F2 were reduced after the 6-month (Table 1). Depletion of the As(V) mass in quickly immobilizing labile fractions (e.g., F1 an F2) followed by time-limited transformation to more recalcitrant fractions (e.g., F4 and F5) could be one important reason for a biphasic immobilization pattern.

The temporal change of labile As(V) concentration was well fitted with the two-domain first-order kinetic model ($r^2 > 0.95$, Table 1). In general, the k_{fast} and F_{fast} measured for the MS-amended samples were greater than those for the SS-amended samples. In all cases, the magnitude of k_{fast} was always > 1.5-order greater than that of k_{slow}, and the F_{fast} values were 0.149–0.710, both of which are indicating kinetically limited immobilization in the amended mine soils. Interestingly, temporal change of individual F1 and F2 was also respectively well fitted with the two-domain model. In general, both k_{fast} and F_{fast} of the F1 fraction were no less than those in the F2 fraction, whereas k_{slow} showed no trend among samples. The k_{fast} of the MS-amended samples was greater than that of the SS-amended samples.

3.3. Dose and timing of amendment application

The effect of amendment dose and timing of addition on immobilization was further assessed in two MS-amended samples (e.g., S2 and M2) whose As(V) contamination levels are about mid-range among six mine soils. For two samples, the initial 5% addition was compared with the initial 2.5% and second 2.5% addition at third month. As shown in Fig. 1, the lability reduction was less for the initial 2.5% addition than that of the 5% addition until 3-month as expected from lower As(V)/ amendment mass ratio of the former. However, labile As(V) concentrations decreased dramatically (>30%, white circles in Fig. 1) upon adding the second 2.5%-MS, and was slightly lower than the

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result for the 5% addition (black circles in Fig. 1). In comparison with the initial 2.5% addition, immobilization (%) per unit mass of amendment approximately doubled for the second 2.5% addition; from 5.2 to 12.8 and from 7.8 to 15.0 for the S2 and M2 samples, respectively. The observation indicates that second 2.5% amendment showed higher of As(V) immobilization efficacy compared with initial 2.5% amendment. The reduced quantity of labile As(V) to react with the freshly added 2.5% amendment at the time of the second addition appeared to enhance the performance.

Table 1. Kinetic parameters[a] for temporal change of As(V) concentration in labile fraction for amendment-treated mine soils over the 6-month experimental period.

Soil	Amendment [b]	Change of Labile As(V) Concentration in Amended Sample				
		k_{fast} ($month^{-1}$) [c]	k_{slow} ($month^{-1}$) [c]	F_{fast} (unitless) [d]	r^2 [e]	Immobilization (%) [f]
S1	MS	0.971 (0.230)	0.036 (0.060)	0.326 (0.059)	0.952	44.2 (6.5)
	SS	0.558 (0.140)	≅0	0.327 (0.102)	0.948	30.2 (5.2)
S2	MS	1.022 (0.148)	≅0	0.558 (0.049)	0.998	55.0 (8.2)
	SS	1.388 (0.501)	0.024 (0.009)	0.149 (0.038)	0.988	24.4 (4.2)
S3	MS	1.262 (0.148)	0.007 (0.015)	0.566 (0.034)	0.998	57.7 (5.1)
	SS	1.665 (0.029)	0.035 (0.001)	0.405 (0.003)	1.00	50.0 (3.2)
M1	MS	1.343 (0.264)	0.048 (0.019)	0.397 (0.058)	0.995	52.7 (3.5)
	SS	0.967 (0.314)	≅0	0.434 (0.175)	0.954	42.1 (5.1)
M2	MS	0.862 (0.168)	≅0	0.710 (0.096)	0.996	69.3 (7.2)
	SS	1.090 (0.014)	0.001 (0.001)	0.343 (0.003)	1.00	34.2 (6.2)
M3	MS	1.484 (0.151)	≅0	0.584 (0.026)	0.999	58.0 (3.5)
	SS	0.626 (0.132)	≅0	0.385 (0.071)	0.998	36.4 (2.1)

[a] Result of the two-domain first-order decay model fit.
[b] The MS and SS denotes mine discharge sludge and steel making slag, respectively.
[c] The k_{fast} and k_{slow} denote the immobilization rate constant for fast-immobilizing and slow-immobilizing domains, respectively. Values in parentheses are standard errors of the fitted value. The sign "≅0" indicates a k_{slow} value $< 1 \times 10^{-15}$.
[d] The fraction of As(V) present in the fast-immobilizing domain.
[e] The goodness of the model fit.
[f] The percent of reduced labile As(V) mass after the 6-month incubation relative to the initial values. Standard deviation of average immobilization (%) is shown in the parentheses.

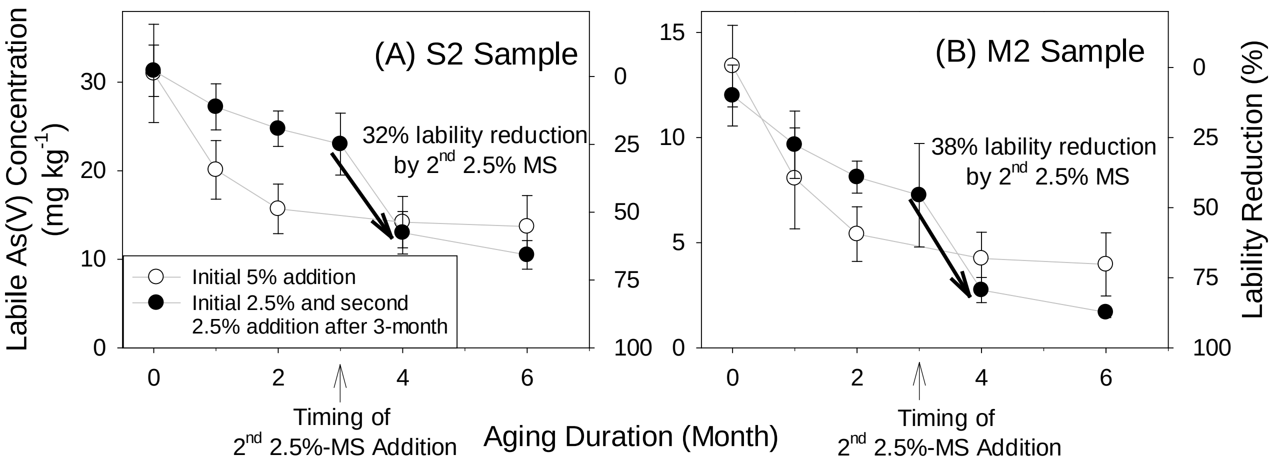


Figure 1. Change of labile As(V) concentrations from the S2 and M2 samples over the 6-month experimental period in the different amendment doses and the timing of addition. The white circle denotes data for initial 5%-MS addition, whereas the black circle denotes data for initial 2.5%-MS addition followed by second 2.5%-MS addition after the lapse of 3-month.

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4. CONCLUSION

The results of this study indicate that the degree of As(V) immobilization is essentially determined by the abundance of clay and amorphous and crystalline Fe/Al oxides available to react with labile As(V) in solid phase. However, these data are insufficient to account for the variation in the immobilization rate (k_{fast} and k_{slow}) among the different soils. All As(V) present in the labile fractions was not simultaneously available for immobilization. Limited accessibility of labile As(V) to the amendment materials (or vice versa) could lead to kinetic variability in the immobilization reaction. In addition, immobilization (%) did not increase linearly with amendment dose; thus, enhanced immobilization can be further attained by adjusting the dose and timing of amendment application. The immobilization method should be designed to build up the soil's capacity (e.g., the pool of F3) to sufficiently accommodate immobilized As(V) to ensure its stability attained by amendment treatments.

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Effects of metal concentration on bacterial inactivation in plasma-activated water

T. Chen[1*], T. Su[1], J. F. Liang[2]

[1]Department of Civil, Environmental and Ocean Engineering, Stevens Institute of Technology, 07030, Hoboken, NJ, USA.
[2]Department of Chemistry, Chemical Biology, and Biomedical Engineering, Stevens Institute of Technology, 07030, Hoboken, NJ, USA.
*Corresponding author: Email: t1su@stevens.edu

Abstract

Non-thermal microhollow cathode discharge in close water surface can generate acidified plasma-activated water (PAW). The antibacterial activity of PAW against *Escherichia coli* show that PAW can effectively inactivate bacteria. From the experimental results, *Escherichia coli* were completely inactivated after 30 minutes of exposure to PAW, and more than 99% of *Staphylococcus aureus* within biofilm were inactivated after 3 hours of contact to PAW. Inductivity Couple Plasma Optical Emission Spectrometry and antibacterial/anti-biofilm activity assay results show that one of the key factors of inactivation of bacteria is induced by copper and zinc ions/complexes in PAW.

Keywords: non-thermal plasma; antibacterial activity; metal complexes; plasma-activated water

1. INTRODUCTION

Non-thermal or low-temperature plasmas can be created under atmospheric conditions and are widely used on material surfaces and in liquids for the killing or inactivation of bacteria, micro-organisms and spores [1, 2]. Many groups have demonstrated that non-thermal/low-temperature plasmas can be used to generate 'plasma-activated solution' by treating solutions under specific conditions, which can be applied to a disinfectant to kill bacteria on contaminated solid surfaces or liquids. They also show that the efficient antimicrobial agents in the plasma-activated solutions are free radicals species. Some groups (M. Pavlovich et. al., and G. Kamgang-Youbi et. al.,) have already shown that the principle species are OH and NO radicals when plasma is generated by use of air as the working gas at atmospheric pressure. It is shown that those OH and NO radicals are responsible for the antimicrobial effect [3-8]. When those reactive species are dissolved in the liquids, those long-lived products, such as H_2O_2 (hydrogen peroxide), NO_3^- (nitrate), NO_2^- (nitrite) and $ONOO^-$ (peroxynitrites) anions, as well as other species are effective in killing or inactivating bacteria. Plasma-activated solution can be used as a disinfectant to contaminated solid surface and liquid. Recent results also show that the antimicrobial capacity of plasma-activated solution can persist as a bactericidal for a couple of days or more [2, 4].

However, the measured concentrations of nitrate, nitrite, H_2O_2, and peroxynitrites were too low to be considered as key bactericidal agents [9]. A possible explanation of the demonstrated enhancement of the antimicrobial activity in the plasma treated solutions might be attributed to a potential presence of metal (copper and zinc) ions/complexes sputtered from the brass cathode during the discharge treatment.

The antimicrobial efficacy of metal ions/complexes against bacteria has been widely reported. These mechanisms indicate that metal ions/complexes can attach to the bacterial cell wall and destroy the bacterial cell wall to increase membrane permeability, and ions are released, proton

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motive force became friable, then intracellular components are effluence. The metal ions/complexes could couple with protein denaturation causing cell lysis and death [10,11].
The objective of this study was to determine the amount of copper (Cu) and zinc (Zn) ions/complexes generated in the PAWs, evaluate the antibacterial activity and anti-biofilm activity of PAWs and copper and zinc ions/complexes.

2. MATERIALS AND METHODS

The crystal violet (CV), 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide (MTT), and tryptic soy broth supplemented with 0.2% glucose (TSBG) was purchased from the Sigma-Aldrich (St Louis, MO). *Escherichia Coli* (ATCC 25404, gram-negative) and *Staphylococcus aureus* (ATCC 29213, gram-positive) were purchased from the American Type Culture Collection (ATCC, Manassas, VA).

2.1 Preparation of plasma-activated water

A non-thermal microhollow cathode discharge (MHCD) device was used in this study. The MHCD was operated at atmospheric pressure by using Air/Oxygen as working gas. The gas flow, discharge power were controlled at 4 liter per minute and 100 Watts, respectively. During this study, we used deionized water (D.I. water) to generate plasma-activated water. Discharge plasma was generated by fixing the discharge probe 5.0 mm above the surfaces of D.I. water in 50-mL conical tubes (Figure 1). After exposure to plasma for specified treatment time (10 minutes and 30 minutes), those PAWs were collected in 15-mL conical tubes and stored in the refrigerator.

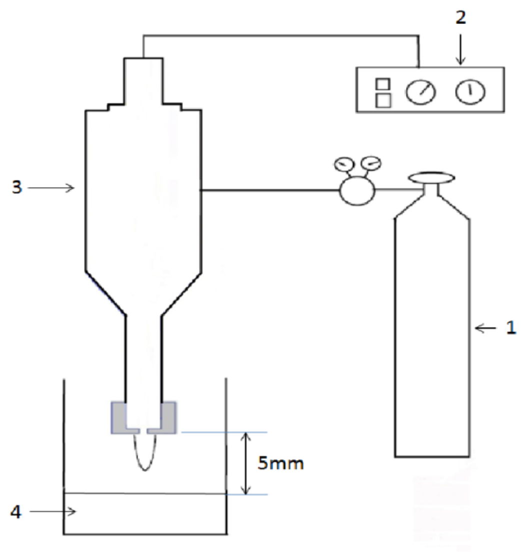


Figure 1.
Schematic diagram of the microhollow cathode discharge (MHCD) device and experiment setup. (1) Gas cylinder; (2) DC power supply; (3) MCHD plasma torch; (4) D.I. water. Discharge plasma is created by gas flowing into the MHCD plasma torch and ejecting plasma toward the surface of the solution.

2.2 Antibacterial activity assay

In the assay, 990 µL of PAW was mixed with 10 µl of midlogarithmic (mid-log) phase bacteria (~ 2 × 10^6 cells·mL^{-1} suspended in TSBG medium). After incubation at room temperature for 30 minutes, a 100 µL of above mixed bacteria suspension was added to a 100 µL of TSBG medium and then cultivated at 37°C incubator overnight. The optical density (OD_{570nm}) of bacterial growth in the TSBG medium was measured using a microplate reader [12].

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2.3 Detection of copper and zinc metal ions/complexes concentration within plasma-activated water

The concentration of copper and zinc within PAWs was detected by Inductively Couple Plasma Optical Emission Spectrometry (ICP-OES). ICP-OES measures light emitted at element specific wavelength from thermally excited analyte ions and atoms. The intensity of this emit electromagnetic radiation can be converted elemental concentration by comparison calibrated reference standard..

2.4. Biofilm growth

An overnight culture of *S. aureus* was diluted in TSBG to 2×10^6 cells·mL^{-1}, and inoculated on 24-well polystyrene cell culture plates for MTT and CV staining assay. The biofilms of *S. aureus* (15–20 µm in thickness) were formed on all tested materials within 24 hours. At the end of incubation, the formed biofilms were washed with phosphate-buffered saline (PBS) solution to remove planktonic and loosely attached bacteria [15, 16].

2.5 Anti-biofilm activity assays

Biofilms were exposed to various PAWs or solution contained 30ppm of Cu and Zn then incubated at room temperature. At the end of treatments, two methods, CV staining and MTT assay, were used to assess biofilm susceptibility to PAWs and solution contained 30ppm of Cu and Zn. The CV staining is used for staining bacterial cells (both live and dead) and other macromolecules such as polysaccharides, DNA, and proteins in biofilm extracellular matrix. The MTT assay was designed for live bacteria by measuring the overall metabolic activity of bacterial cells in biofilms. There is an excellent correlation between formazan concentrations (absorbance at OD 570 nm) and CFU counting [12]. Thus, CV staining was used for the quantification of biofilms (total biomass) while MTT assay was utilized to evaluate the viability of bacteria in biofilms.

In CV staining, biofilms were stained with 0.1% (w/v) CV for 10 minutes. The excess dye was removed by thoroughly rinsing the plate with D.I. water. Then, CV dye associated with biofilms was then extracted by 33% glacial acetic acid for quantification by using a microplate reader. The absorbance of solution was measured at 570 nm [16]. In the MTT assay, treated biofilms were washed with D.I. water to remove residual PAWs and solution contained 30ppm of Cu and Zn then incubated with 5% (W/V) MTT at 37ºC for 10 minutes. A sodium dodecyl sulfate (SDS) solution was used to dissolve the purple formazan that formed inside the bacterial cells then measured optical density values with microplate reader by setting the detecting and reference wavelengths at 570 nm and 630 nm, respectively [17].

3. RESULTS AND DISCUSSION

3.1 The plasma-activated water's pH and antibacterial ability

One of the most notable consequences of plasma exposure to the solution is dramatically decreased solution pHs, many studies were conducted in acidic (pH~3.7) [2-5, 13-14]. The results of pH change occurred from 6.8 to 2.55 in PAW-Air-10 (Plasma-activated water generated by using air to treat 10 minutes), and the pH of PAW-O2-10 (plasma-activated water generated by using oxygen to treat 10 minutes) was 2.80. However, with increasing plasma exposure time to the D.I. water, the pH change was imperceptible (Figure 2a).

The results of *E. coli* disinfection experiments with PAW-Air-10, PAW-Air-30, PAW-O2-10, and PAW-O2-30 are shown in Figure 2b. In Figure 2b, the *E. coli* was completely inactivated after 30 minutes exposed with PAW-Air-30, and PAW-O2-30. However, the PAW-Air-10, and PAW-O2-10 was inactivated slightly.

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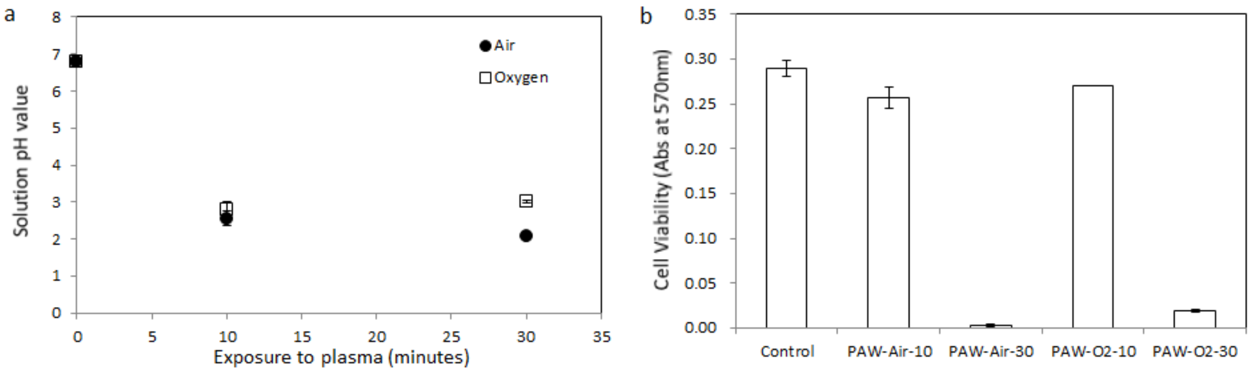


Figure 2. (a) Plasma induced D.I. water pHs changes with various working gases. (b) Antibacterial activity of plasma-activated waters tested on *E. coli*.

3.2 Concentration of metal ions/complexes

Some groups (M. Pavlovich et al., and G. Kamgang-Youbi et al.) shown that nitrate, nitrite, hydrogen peroxide, and peroxynitrites maybe the key factors to kill or inactivate bacteria; however, the measured concentrations were too low to be considered as key bacterial agents [9]. After each experiment, we found that the electrically-conductive tube (cathode, brass material) was sensitive to corrosion (Figure 3). This is possible to attribute to the antimicrobial activity in the PAWs due to a potential presence of metal (copper and zinc) ions/complexes during the discharge treatment.

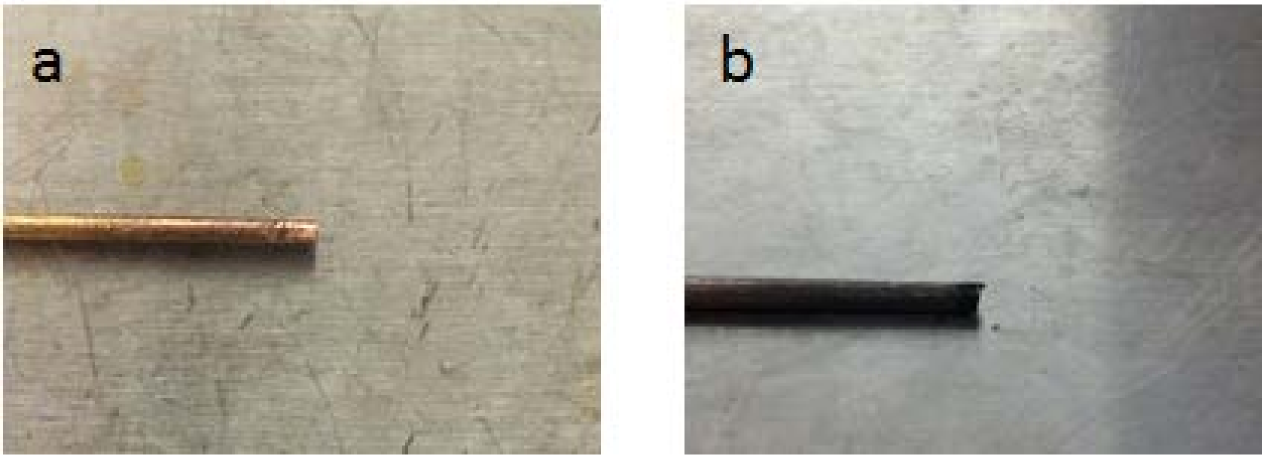


Figure 3. Photographs of electrically-conductive tube (a) before, and (b) after used.

Figure 4 shows the copper and zinc ions/complexes amount (ppm) in the PAWs, which was measured by ICP-OES. In the PAW-Air-10, the concentration of Cu and Zn both increased from 0 to 7.0ppm and 6.5ppm respectively within 10 minutes plasma treatment. The content of Cu and Zn increases continuously with increasing treatment time. After 30 minutes plasma treatment, the Cu and Zn concentration increased to 51.7ppm and 31.6ppm, respectively. In the PAW-O2-30, the concentrations were measured 34.5ppm of Cu, and 15ppm of Zn. We also found that the ratio of Cu and Zn was between 1 and 2.5.

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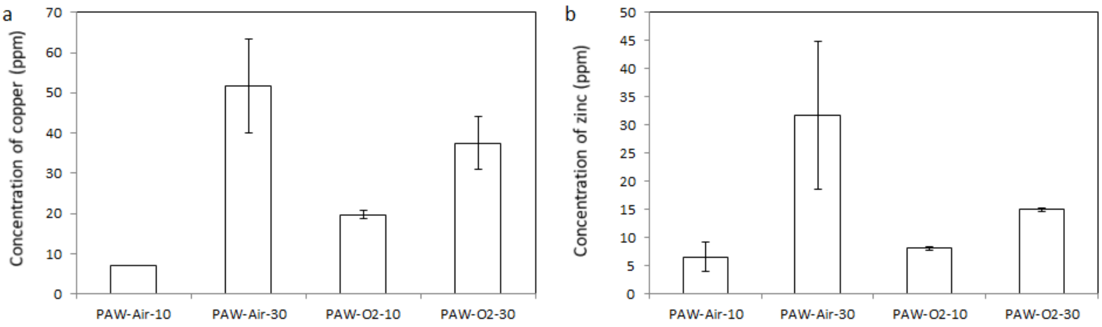


Figure 4. Concentration of metal ions/complexes was generated within the PAWs. Emergence of (a) copper and (b) zinc ions/complexes were measured by ICP-OES with various gases and exposure time.

3.3 Antibacterial ability of metal ions solution

From previous assay, we would like to determine whether metal concentration is responsible for antibacterial activity. In this work, we prepare two different ratios (1:1 and 2.5:1) of Cu and Zn solutions to evaluate its antibacterial effects. Figure 5 shows the antibacterial efficacy when *E. coli* was exposed to various concentrations of Cu and Zn at 37°C incubator for 30 minutes. After treatment, we found that the Solution 1 at concentration 15ppm of Cu and Zn and the Solution 2 at concentration 30ppm of Cu and 12ppm of Zn had the sufficient efficacy to completely inactivate *E. coli*. These results also confirmed PAW antibacterial activity results.

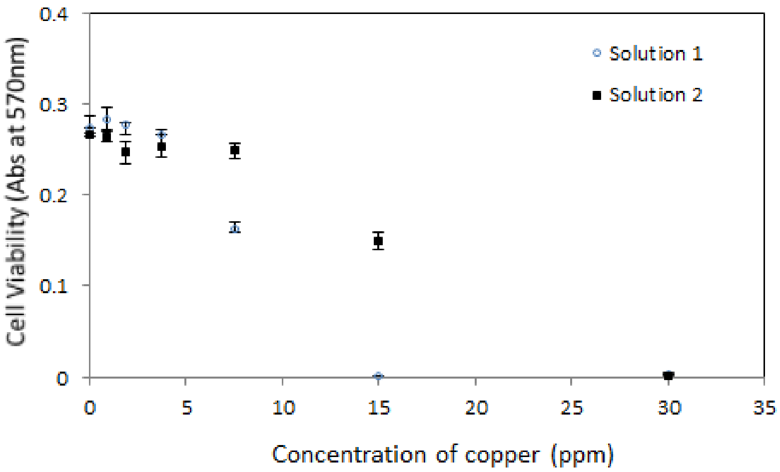


Figure 5. Antibacterial activity of various concentrations of mixed copper and zinc ion solutions tested on *E. coli*. Solution 1, the concentration ratio of copper ions to zinc ions is 1 to 1, and Solution 2, the concentration ratio of copper ions and zinc ions is 5 to 2.

3.4 Anti-biofilm activity assay

One of the most important features of biofilms is their resistant nature towards chemical and antimicrobial treatments [18-20]. However, biofilms are sensitive to plasma and bacteria in mature biofilms of various sizes are killed completely by directly exposing biofilms to gas discharge plasma [15-17, 21-22]. Motivated by the excellent anti-biofilm activity of plasma, we tested the capability of solution contained 30ppm of Cu and Zn and PAWs in biofilm inactivation. In agreement with their good antibacterial abilities, solution contained 30ppm of Cu and Zn and PAWs demonstrated strong anti-biofilm activity (Figure 6a). After 3 hours contact time, PAW-O2-30 can

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inactivate around 99% of bacteria within the 1-day old biofilm, and more than 99.9% of bacterial cells in 1-day old biofilms were killed with solution contained 30ppm of Cu and Zn and PAW-Air-30. Studies on plasma mediated biofilm inactivation revealed that the observed anti-biofilm activity of plasma attribute to the antibacterial and etching capability of plasma [15]. Reactive species generated in plasma can damage biofilm extracellular matrix to release bacteria and biofilm debris from attached surfaces. However, PAWs and solution contained 30ppm of Cu and Zn are deprived of biofilm etching function. Despite completely inactivated bacteria, biofilms treated with PAWs and solution contained 30ppm of Cu and Zn maintained the same biomass as the controls after long time incubation (Figure 6b). This result supports the conclusion that maybe metal ions/complexes are responsible for the antibacterial and anti-biofilm.

Reasons for biofilm resistance include limited nutrition diffusion and mutant development in biofilms. The excellent activity of plasma attributes to the good biofilm permeability and cell membrane-disrupting capability of discharge gases [15, 17]. Extended contact time is required to complete biofilm inactivation in comparison with planktonic cells (3 hours vs. 30 minutes), reflecting the slow diffusion of PAW into biofilms.

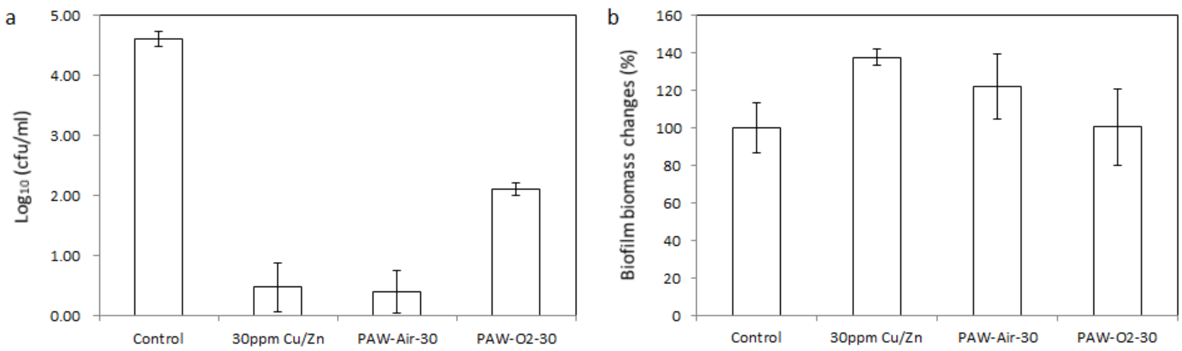


Figure 6. Plasma-activated waters and solution contained 30ppm of Cu and Zn induced (a) bacteria inactivation (b) biomass change in 1-day old *S. aureus* biofilms.

4. CONCLUSIONS

The following can be concluded from this study:

- Plasma treatment caused the acidification of D.I water, and it showed the pH changes from 6.8 to around 2.5 after 10 minutes of plasma treatment.
- The PAWs showed excellent inactivation activity. The bacteria were unable to survive in PAWs after an exposure of 30 minutes.
- ICP-OES information showed that metal (Cu and Zn) ions/complexes were present in the PAWs. Cu and Zn ions/complexes could possibly be sputtered from the brass cathode during the discharge generated.
- Cu and Zn ions/complexes not only exhibited great antibacterial properties against the pathogen *E. coli*, but also showed impressive anti-biofilm activities. Cu and Zn ions/complexes likely act in the key role in the PAWs for bacterial/biofilm inactivation.

References

[1] Ikawa S., Kitano K., Hamaguchi S., 2010. Effects of pH on bacterial inactivation in aqueous solutions due to low-temperature atmospheric pressure plasma application. *Plasma Processes and Polymers*, **7(1)**, 33-42.

[2] Pavlovich M.J., Chang H., Sakiyama Y., Clark D.S., Graves D.B., 2013. Ozone correlates with antibacterial effects from indirect air dielectric barrier discharge treatment of water. *Journal of Physics D: Applied Physics*, **46(14)**, 145202-145211.

ISBN: 978-960-6865-94-7

[3] Kamgang-Youbi G., Herry J.-M, Brisset J.-L., Bellon-Fontaine M.-N, Doubla A., Naïtali, M., 2008. Impact on disinfection efficiency of cell load and of planktonic/adherent/detached state: case of *Hafnia alvei* inactivation by plasma activated water. *Applied Microbiology and Biotechnology*, **81(3)**, 449-457.
[4] Traylor, M.J., Pavlovich, M.J., Karim, S., Hait, P., Sakiyama, Y., Clark, D.S., Graves, D.B., 2011. Long-term antibacterial efficacy of air plasma-activated water. *Journal of Physics D: Applied Physics*. **44(47)**, 472001.
[5] Naïtali, M., Kamgang-Youbi, G., Herry, J.-M., Bellon-Fotaine M.-N., Brisset, J.-L., 2010. Combined effects of long-living chemical species during microbial inactivation using atmospheric plasma-treated water. *Applied and Environmental Microbiology*, **76(22)**, 7662-7664.
[6] Kamgang-Youbi, G., Herry, J.-M., Meylheuc, T., Brisset, J.-L., Bellon-Fontaine, M.-N., Doubla, A., Naïtali, M., 2009. Microbial inactivation using plasma-activated water obtained by gliding electric discharges. *Letters in Applied Microbioligy*, **48(1)**, 13-18.
[7] Kamgang-Youbi, G., Naïtali, M., Herry, J.-M., Hnatiuc, E., Brisset, J.-L., 2010. Direct and post-discharges in environmental applications of cold plasmas. *Proceeding of the 12th International Conference on Optimization of Electrical and Electronic Equipment (OPTIM)*, May 20-22, Brasov, Romania, 1336-1342.
[8] Kamgang-Youbi, G., Herry, J.-M., Bellon-Fontaine, M.-N., Brisset, J.-L., Doubla, A., 2007. Evidence of temporal postdischarge decontamination of bacteria by gliding electric discharges: application to *Hafnia alvei*. *Applied and Environmental Microbiology*, **73(15)**, 4791-4796.
[9] Machala, M., Tarabova, B., Hensel, K., Spetlikova, E., Sikurova, L., Lukes, P., 2013. Formation of ROS and RNS in water electron-sprayed through transient spark discharge in air and their bactericidal effects. *Plasma Processes and Polymers*, **10(7)**, 649-659.
[10] Méndez-Vilas A., 2011. Science against microbial pathogens: communicating current research and technological advances. 3rd ed., Formatex Research Center, Spain.
[11] Lin, Y.E., Vidic, R.D., Stout, J.E., Yu, V.L., 1996. Individual and combined effects of copper and silver ions on inactivation of *Legionella pneumophila*. *Water Research*, **30(8)**, 1905-1913.
[12] Kharidia, R., Liang, J.F., 2011. The Activity of a Small Lytic Peptide PTP-7 on *Staphylococcus aureus* Biofilms. *The Journal of Microbiology*, **49(4)**, 663-668.
[13] Ercan, U.K., Wang, H., Ji, H., Fridman, G., Brooks, A.D., Joshi, S.G., 2013. Nonequilibrium plasma-activated antimicrobial solutions are board-spectrum and retain their efficacies for extended period of time. *Plasma Processes and Polymers*, **10(16)**, 544-555.
[14] Zhang, Q., Liang, Y., Feng, H., Ma, R., Tian, Y., Zhang, J., Fang, J., 2013. A study of oxidative stress induced by non-thermal plasma-activated water for bacterial damage. *Applied Physics Letters*, **102(10)**, 203701.
[15] Traba C., Liang, J.F., 2011. Susceptibility of *Staphylococcus aureus* biofilms to reactive discharge gases. *Biofouling*, **27(7)**, 763-772.
[16] Traba, C., Chen, L., Liang, J.F., 2013. Low power gas discharge plasma mediated inactivation and removal of biofilms formed on biomaterials. *Current Applied Physics*, **13(Supplement 1)**, S12-18.
[17] Traba, C., Chen, L., Liang, D., Azzam, R., Liang, J.F., 2013. Insights into discharge argon-mediated biofilm inactivation. **Biofouling**, 29(10), 1205-1213.
[18] Patel, R. 2005. Biofilms and antimicrobial resistance. *Clinical Orthopaedics and Related Research*, **437**, 41-47.
[19] NNIS System, 2003. National Nosocomial Infections Surveillance (NNIS) system report, data summary from January 1992 through June 2003, *American Journal of Infection Control*, **31(8)**, 481-498.
[20] Donlan, R.M., 2011. Biofilm elimination on intravascular catheters: important considerations for the infectious disease practitioner, *Clinical Infection Disease*, **52(8)**, 1038-1045.
[21] Joshi, S.G., Paff, M., Friedman, G., Fridman, G. Fridman, A., Brooks, A.D., 2010. Control of Methicillin resistant *Staphylococcus aureus* in planktonic form and biofilms: a biocidal efficacy study of nonthermal dielectric-barrier discharge plasma. *American Journal of Infection Control*, **38(4)**, 293-301.
[22] Joaquin, J.C., Kwan, C., Abramzon, N., Vandervoort, K., Brelles-Marino, G., 2009. Is gas discharge plasma a new solution to the old problem of biofilm inactivation? *Microbiology*, **155**, 724–732.

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Ecotoxicology

PROTECTION
AND
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OF THE
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XIII

Ecotox-scores as a cost-effective and robust method to evaluate the environmental risk of PAHs polluted soils

C. Lors[1,2*], J. F. Ponge[3], D. Damidot[1,2]

[1] Mines Douai, LGCgE -GCE, 941 rue Charles-Bourseul, 59508 Douai, France.
[2] Université Lille Nord de France, 1bis rue Georges Lefèvre, 59044 Lille Cedex, France.
[3] Muséum National d'Histoire Naturelle, CNRS UMR 7179, 4 Avenue du Petit-Château, 91800 Brunoy, France.
* Corresponding author: Email: christine.lors@mines-douai.fr

Abstract

It is necessary to complement the chemical analysis by ecotoxicity bioassays which proved to be more sensitive indicators of soil quality. Ecotox-score calculated from a battery of specifically selected liquid and solid phase bioassays appeared to be a cost-effective and robust method to classify soils according to their toxicity level. Indeed, ecotox-scores were able to discriminate two coke factory soils contaminated with a similar total concentration of PAHs. The combination of chemical and toxicological data highlighted the relationship between acute ecotoxicity and 3-ring PAHs. The chronic effect of both water extracts on algal growth could be explained by high molecular weight PAHs, such as 5- and 6-ring PAHs. Ecotox-score can be a cost-effective assessment of PAHs polluted/remediated soils complementary to chemical analysis.

Keywords: soils; PAHs; ecotoxicity; ecotoxicological test battery; bioavailability; Ecotox-scores

1. INTRODUCTION

Industrial activities have led to the discharge of a wide range of hazardous chemicals in soils. These pollutants include mostly hydrocarbon aromatic hydrocarbons (PAHs) and heavy metals. PAHs are a group of persistent organic pollutants that are generally formed by the incomplete combustion of fossil fuels, coal liquefaction, creosote production and petroleum refining [1]. PAHs are a major environmental and health concern because of their potentially toxic, mutagenic and carcinogenic properties [2]. PAHs can adversely affect not only human health but also terrestrial and aquatic ecosystems. Hazard risk assessments of polluted soils are usually performed by chemical analysis to determine concentrations of target compounds. However, chemical analysis does not allow to identify all the compounds, but only to quantify those which are to be analysed. Moreover, it does not provide information on the bioavailability of pollutants, neither on synergic or antagonistic phenomena between pollutants, nor on their effect on living organisms. In the case of PAHs that are hydrophobic organic pollutants, they may be adsorbed onto soil matrices and thus be less bioavailable [3]. Soil properties, such as organic matter content, and its ageing also play an important role in the bioavailability of PAHs [4,5]. So, these parameters can significantly affect their fate in ecosystems and their impact on species and population [6]. As a consequence, a battery of bioassays involving organisms at different levels of biological organization and accounting for acute/chronic ecotoxicity or genotoxicity is recommended to evaluate the environmental hazard of contaminated soils.

Different approaches were performed to assess soil ecotoxicity: bioassays on whole soil using bacteria, earthworms, collembolans and plants [7], liquid bioassays applied on both water and organic extracts [8] and combinations of both bioassays on whole soil and on soil water extracts [9,10]. Direct toxic effects on terrestrial organisms may reflect the ecotoxicological potential of

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contaminated soils [11,7] whereas soil organic extracts may lead to an overestimation of the real bioavailability of organic pollutants [12].

The first goal of this work is to demonstrate that chemical analyses were not sufficient to evaluate the hazard of polluted soils and these analyses have to be complemented by ecotoxicity bioassays.

The second goal is to confirm the robustness of a method previously defined by Lors et al. [13], in order to evaluate the environmental risk through the calculation of an ecotox-score. This method relies on an optimised battery of solid- and liquid-bioassays that gave satisfactory results from the viewpoint of ecological relevance [13]. It was thus applied in the present article, to two historical contaminated soils presenting a similar total concentration of PAHs in order to check its robustness. Additionally, the combination of chemical and toxicological data was used to bring some new insights between ecotoxicity and the different types of PAHs.

2. MATERIALS AND METHODS

2.1 Soil samples

Experiments were carried out on two contaminated soils, named soils A and B, sampled from two historical industrial sites located in the North of France. Soil A was sampled in the untreated site whereas Soil B underwent a windrow treatment for 18 months. Despite bioremediation, this soil was still polluted with PAHs, with a total concentration still around that of Soil A. Unpolluted soils were sampled in the two studied sites in uncontaminated areas. These soils were used as controls in the avoidance test and as a dilution matrix in solid-phase bioassays. The procedure used for soil sampling has been described by Lors et al. [7].

2.2 Water extraction of soil samples

Soil water extraction was carried out according to [14] without any preliminary filtration: liquid:solid ratio 10:1 (170 g of soil in 1.7 L of distilled water) at 20°C in 2 L glass bottles for 24 h at a stirring rate of 60 rpm. After decanting for 15 min, the soil suspension phase was centrifuged at 2,000 g during 30 min and stored at 4°C until chemical and ecotoxicological analyses.
PAH-releasing capacity is expressed by the ratio between PAH-concentration in water extract (per unit mass of soil for water extraction) and PAH-concentration in soil.

2.3 Chemical analyses

Concentrations of the 16 PAHs of the US-EPA list [15] were dosed in soils and water extracts according to ISO 13877 [16]. The separation of PAHs from water extracts was conducted with dichloromethane. The extraction of PAHs from soil samples was carried out with the solvent extractor system Dionex® ASE 200 (Dionex Corporation®, Sunnyvale, CA), allowing a procedure described by Lors et al. [13]. PAHs were separated in a column (Supelco® C18 reverse phase, length 250 mm, internal diameter 2.1 mm) using a gradient of acetonitrile/water solvent. PAHs analyses were also carried out in soil water extracts by HPLC (Waters® 2690, Milford, MS) coupled to a fluorescence detector. The ratio between PAH concentration in water extract and in soil allowed determining the PAHs water extraction capacity of the studied soils. PAHs analyses in both soils and water extracts were done in triplicate.

2.3. Ecotoxicological analyses

The toxicity of soils was evaluated with the bioassays selected by Lors et al. [13], including two rapid bioassays (Microtox® and springtail avoidance), a micronucleus test and three bioassays of a longer duration (algal growth, lettuce germination and springtail reproduction).

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Bioassays applied directly on soil included an acute toxicity bioassay like phytotoxicity tests on *Lactuca sativa* [17] and an chronic toxicity bioassay based on springtail (*Folsomia candida*) reproduction according to ISO 11267 [18] modified by Martínez Aldaya et al. [19]. An avoidance test was conducted on *Folsomia candida* according to Martínez Aldaya et al. [19] and Lors et al. [20]. Detailed procedures of these bioassays were described by Lors et al. [7]. The pH of both soils was around 8 and thus was compatible with requirements of test organisms.

The toxicity of water extracts to aquatic organisms was assessed through both acute and chronic effects. The protocol of each bioassay was detailed by Lors et al. (2011) [13]. An acute ecotoxicity test was performed by measuring the inhibition of bioluminescence of the bacterium *Vibrio fischeri* according to ISO 11348-3 [21]. Chronic ecotoxicity was evaluated on growth of the fresh water alga *Pseudokirchneriella subcapitata* according to ISO 8692 [22] The pH of the water extracts was close to 8 for all soils studied, which is compatible with the validity domain of toxicity tests performed in the present study. The in vitro micronucleus assay was performed according the procedure described by Nesslany and Marzin [23]. This micro-method used mouse lymphoma cells L5178Y. The micronucleus assay was performed with and without S9 metabolic activation using the 9000 g cell supernatant from livers of Aroclor 1254-treated rats.

2.5. Calculation of ecotox-scores

Toxic effects were calculated as percentages of inhibition at a given concentration or as LE_{Cx} values. Percent inhibition was determined with respect to the control soil. LE_{Cx} values were calculated following adjustment of data to a log-probit logistic model [24]. NOEC was the highest concentration tested that did not significantly differ from control with a type I error (α) of 5%. LOEC was not used and was replaced by EC_{10} or LC_{10}. Toxicity values were also expressed in Toxic Units (TU), using the formula TU = 100/EC(or LC)$_{50}$.

A bioassay-score was calculated for each bioassay as the mean value of the scores obtained from four ecotoxicological parameters; $E(L)C_{50}$, $E(L)C_{20}$, $E(L)C_{10}$, NOEC. A score of 0, 33, 67 or 100 was given as a function of the intensity of the ecotoxicological parameters (x) considered:

- 0 = no effect ($x>100$)
- 33 = weak effect ($50<x\leq100$)
- 67 = medium effect ($20<x\leq50$)
- 100 = strong effect ($x\leq20$)

It has to be noticed that the scale of the scores was modified compared to Lors et al. [7] in order to normalize to 100 the maximum effect. Finally, the ecotox-score was then calculated as the mean value of the bioassay scores obtained for each bioassay performed. The following scale was used to define the environmental risk of PAHs polluted soils:

- no toxicity (ecotox-score = 0)
- weak toxicity (0 < ecotox-score ≤ 33)
- moderate toxicity (33 < ecotox-score ≤ 67)
- strong toxicity (67 < ecotox-score ≤ 100)

3. RESULTS AND DISCUSSION

3.1 Chemical and toxicological characteristics of soils

Soil A was mainly contaminated with organic compounds. This soil was heavily polluted with PAHs, with a global content of about 3 g kg^{-1} dry soil, mainly represented by 2-, 3- and 4-ring compounds. Three-ring PAHs were the most represented (44% of ∑ 16PAHs), followed by 2- and 4-ring compounds (28 and 20 %, respectively) (Figure 1). Five- and 6-ring PAHs were hardly present in this soil (5 and 2 %, respectively).

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Soil B was highly polluted with PAHs, to a level similar to Soil A (∑ 16PAHs= 3.69 g kg^{-1}). However, PAHs distribution pattern was different from Soil A (Figure 1). Four-ring PAHs were the most represented (50% of ∑ 16PAHs – 1727 mg/kg dry soil) followed by 5-ring PAHs (22% – 796.1 mg kg^{-1} dry soil). Contrary to soil A, 3-ring PAHs content was lower, 623.5 against 1279.2 mg/kg dry soil for Soil A. This difference of distribution is probably the consequence of the partial degradation of PAHs during biotreatment that was more efficient to decrease 2- and 3-rings PAHs, as expected [26]. Thus, the concentrations of 4-, 5-, and 6-ring PAHs were higher for Soil B contrary to 2- and 3-ring PAHs.

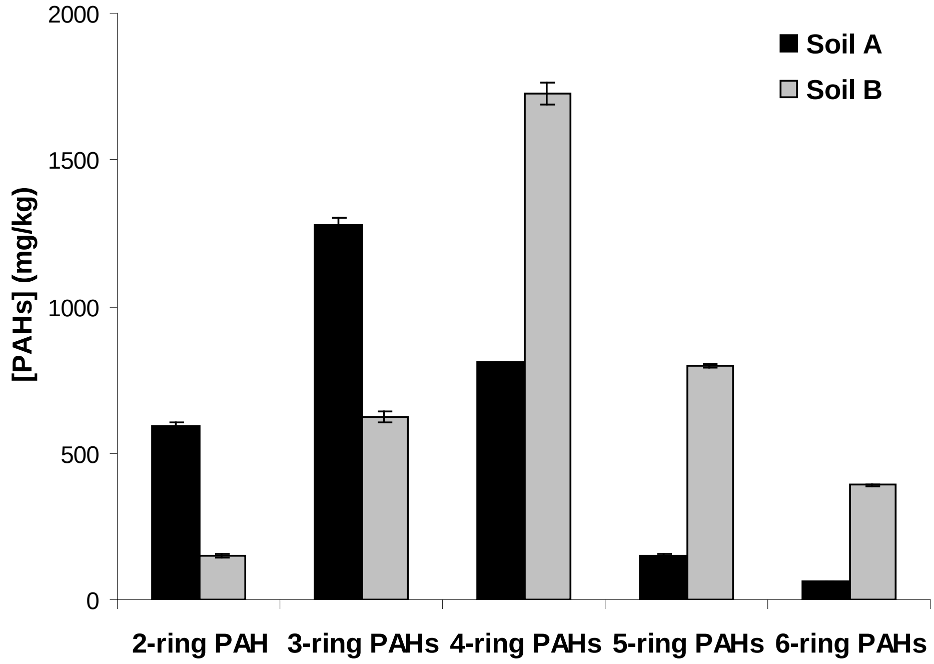


Figure 1. Concentrations of 2-6 rings PAHs in the two studied soils.

Soil A induced a strong inhibition of lettuce germination. At the highest dose tested, the lettuce germination was inhibited to about 70% and the bioassay-score was to 93 (Table 1). Conversely, Soil B showed a significantly lower phytotoxicity towards lettuce germination as its bioassay-score was 47 (Table 1). The *Folsomia* population growth bioassay showed that Soil A had a high chronic ecotoxicity, with an bioassay-score of 100 whereas Soil B exerted any response on *F. candida* population. For Soil B, the behavioural test seemed to be more sensitive than ecotoxicity tests since it allowed to detect a significant repellence (bioassay-score = 67). Nevertheless, the repellence level was lower than that of Soil A (bioassay-score = 100). So, Soil A presented a strong ecotoxicity towards terrestrial organisms whereas the ecotoxicity of Soil B was moderate: ecotox-scores of Soil A and Soil B, obtained with this battery of bioassays, were 98 and 38, respectively.

These results demonstrate that the global content of PAHs is not the pertinent parameter to evaluate soil pollution hazards. Conversely, the distribution of PAHs gave a better picture of soil pollution and it can explain partly the ecotoxic responses obtained. In fact, the high ecotoxicity of Soil A on terrestrial organisms was probably related to its high concentration in 3-ring PAHs. Indeed, a positive and significant relationship between bioassay-scores pooled over the three solid bioassays and the concentration of 3-ring PAHs was found by Lors et al. [7]. Soil A exhibited a high ecotoxicity on organisms tested: plants and Collembola, with bioassay-scores of 93, 100, and 100 to *Lactuca* germination, *Folsomia* population growth and *Folsomia* avoidance respectively (Table 1).

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3.2 Chemical and toxicological characteristics of water extracts

Aqueous leaching tests of soils showed that Soil A had a strong capacity to release PAHs. In fact, the ratio PAH concentration in water extract / soil was equal to 2.2 10^{-3}. The water extract A mainly contained 3-ring PAHs (82% of ∑ 16PAHs – 531.1 µg/L) (Table 2). Their high concentration in solution was linked to their amount in Soil A (1279.2 mg/kg) and the higher solubility of PAHs having lower molecular weights.

Table 1. Ecotox-scores of the two studied soils calculated from the bioassay-scores obtained with three solid-phase bioassays and three liquid-phase bioassays.

		Type of effect	**Soil A**	**Soil B**
Solid phase bioassays	bioassay-score for Lactuca germination	Acute ecotoxicity	93	47
	bioassay-score for Folsomia population growth	Chronic ecotoxicity	100	0
	bioassay-score for Folsomia avoidance	behaviour	100	67
	ecotox-score		98	38
Liquid phase bioassays	bioassay-score for Microtox® test	acute ecotoxicity	100	0
	bioassay-score for Algal growth	acute ecotoxicity	80	80
	bioassay-score for Micro-nucleus test	genotoxicity	80	0
	ecotox-score		87	27
Solid and liquid phase bioassays	ecotox-score		92	32

Table 2. Concentrations of PAHs in water extracts A and B (expressed in µg/L). Water-solubilities of PAHs at 25°C (expressed in µg/kg) were also indicated.

	No. of rings	**Water extract A**	**Water extract B**	**Water-solubility**
Naphthalene	2	0.20 ± 0.02	0.6 ± 0.2	3.2 10^{4}
Acenaphthylene	3	-	-	3.4 10^{3}
Acenaphthene	3	154.1 ± 1.5	0.6 ± 0.1	3.9 10^{3}
Fluorene	3	198.7 ± 3.7	0.7 ± 0.1	2.0 10^{3}
Phenanthrene	3	151.4 ± 2.8	1.4 ± 0.2	1.3 10^{3}
Anthracene	3	26.9 ± 0.4	1.3 ± 0.3	7.3 10^{1}
Fluoranthene	4	51.2 ± 0.9	4.1 ± 0.7	2.6 10^{2}
Pyrene	4	28.9 ± 0.5	3.1 ± 0.6	1.4 10^{2}
Benzo[a]anthracene	4	8.0 ± 0.1	3.1 ± 0.6	1.4 10^{1}
Chrysene	4	8.8 ± 0.1	3.4 ± 0.6	2.0 10^{0}
Benzo[b]anthracene	5	3.85 ± 0.05	8.4 ± 1.4	1.2 10^{0}
Benzo[k]fluoranthene	5	2.30 ± 0.03	2.7 ± 0.5	7.6 10^{-1}
Benzo[a]pyrene	5	4.41 ± 0.02	6.9 ± 1.4	3.8 10^{0}
Dibenzo[ah]anthracene	5	0.72 ± 0.01	3.4 ± 0.6	*2.6* 10^{-1}
Benzo[ghi]perylene	6	3.00 ± 0.03	8.4 ± 1.7	6.2 10^{1}
Indeno[123- *cd*]pyrene	6	2.30 ± 0.04	9.0 ± 1.8	5.0 10^{-1}

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The leaching of PAHs decreased with the number of rings (Figure 2). PAH concentrations in water extracts were correlated to water-solubility of these pollutants. More soluble PAHs, such as acenaphthene, fluorene and phenanthrene, were found at the highest concentrations in water extract A (Table 2). Conversely, four-ring PAHs were present in a lesser proportion (15% of ∑ 16PAHs – 96.9 µg/L), whereas 5- and 6-ring PAHs were not significantly represented in water extract A (1.8 and 0.8 % – 11.3 and 5.3 mg/L respectively) (Table 2).

Soil B released 10 times lower amounts of PAHs than Soil A (1.6 10^{-4}). Five- and 6-rings PAHs were the most represented (respectively 37 and 30 % of ∑ 16PAHs – 21.4 and 17.5 mg/L) (Table 2). Among 5-ring PAHs, benzo(*b*)anthracene and benzo(*a*)pyrene were the major compounds in water extract B. Water extract B also contained 4-ring PAHs in a lesser proportion (23.9% of ∑ 16PAHs – 13.7 mg/L). Three-ring PAHs were also hardly released and thus their concentrations were about 100 times less than water extract A. So, the windrow treatment applied to this soil was efficient because it removed low molecular weight PAHs and the remaining PAHs were the compounds most recalcitrant to microbial degradation [26]. Indeed, Soil B contains essentially 4-, 5- and 6-ring PAHs which were characterized by a weak water-solubility and a high lipophily.

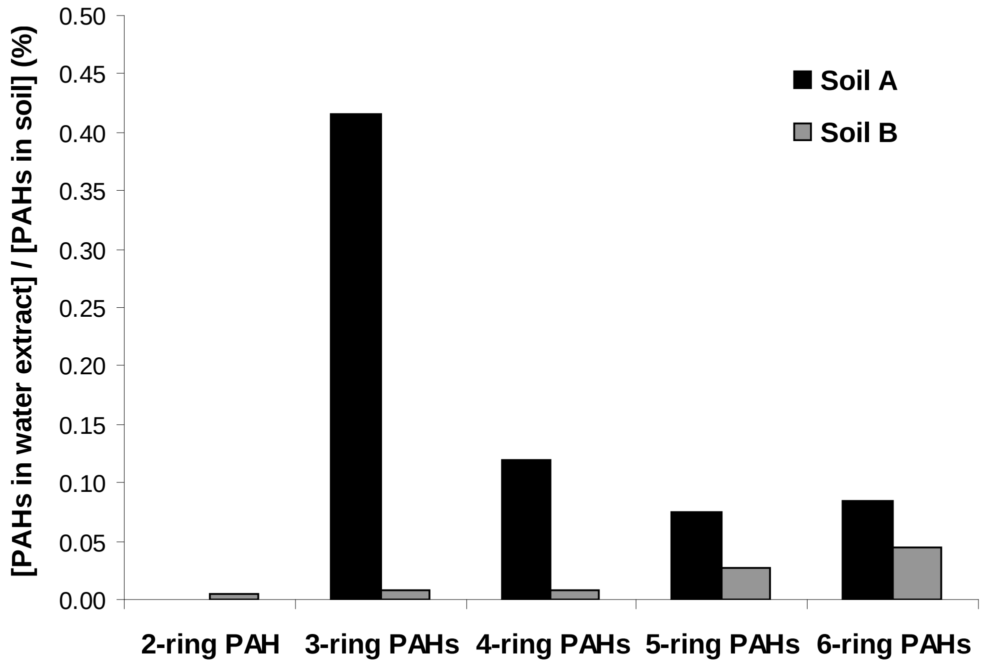


Figure 2. Ratio of PAHs concentration in water extract to concentration in soil (expressed in %) for the two studied soils.

Water extract A exhibited a strong acute ecotoxicity to *Vibrio fischeri* (ecotox-score = 100) (Table 1). Conversely, water extract B did not show any acute ecotoxicity with this bioassay (bioassay-score = 0) (Table 1).These results seemed to be linked to the 3-ring PAHs content in these water extracts: high amount in water extract A (∑ 3-ring PAHs = 644.8 mg/L) and small amount in water extract B ((∑ 3-ring PAHs = 57.3 mg/L) [25]. This confirms the correlation between 3-ring PAHs and acute ecotoxicity observed by Lors et al. [13].

However, the effects of water extracts A and B on algal growth were comparable on the basis of bioassay-scores. Water extracts A and B showed a high chronic response towards *Pseudo-kirchneriella subcapitata* (bioassay-scores of 80 for both soils). These results indicated that both soils had a potential impact to aquatic fauna in the long term and that ecotoxicological effects were due to 5- and 6-rings PAHs, although these were present in lower contents in both water extracts

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(Figure 2). Nevertheless, the ratio between the concentration of each PAH in water extract and its water-solubility was higher than 1 for all 5- and 6-rings PAHs to the exception of benzo[*g*,*h*,*I*]perylene (Table 2). This suggests that high molecular-weight PAHs were associated with other compounds such as suspended organic matter or were in colloidal form, making them bioavailable to aquatic organisms.

The micronucleus test showed a high genotoxicity only without S9 activator (bioassay-score = 80) for water extract A, indicating the presence of directly genotoxic compounds in this water extract. So, the genotoxicity response was not due to PAHs which are known to be activated into genotoxic metabolites by S9 rat liver enzymes. Conversely, any genotoxic effect was observed for water extract B. So, the ecotoxicological approach gave a global response and took into account all potentially toxic compounds and not only those that had been determined by chemical analysis.

The comparison of ecotox-scores calculated both for liquid and solid phase bioassays showed that Soil A was classified as strongly toxic by both types of bioassays. Ecotox-scores were 87 and 98 for liquid and solid phase bioassays respectively. Conversely, Soil B, which was at the limit between weak and moderate effects, appeared weakly toxic by liquid phase bioassays (ecotox-score = 27) and moderately toxic by solid phase bioassays (ecotox-score = 38). This was due to a lower sensitivity of liquid phase bioassays compared to that of solid phase bioassays as showed by Lors et al. [13]. Nevertheless, chemical and ecotoxicological analyses of water extracts were representative of the water-soluble fraction which was directly accessible to organisms. So, the water extract was complementary to the bulk soil in the procedure of hazard assessment. The weak toxicity of soil B compared to the strong toxicity of soil A was also confirmed by the calculation of ecotox-scores using liquid and solid phase bioassays; ecotox-score equals to 32 and 92 respectively (Table 1).

3. CONCLUSIONS

Two coke factory soils contaminated with similar PAHs total concentration were characterized by chemical and ecotoxicological approaches applied on the whole soil and on the water extract. The battery of bioassays including solid and liquid-bioassays took into account acute, chronic and genotoxic effects. The total PAH content of soil was not the more pertinent parameter to assess the hazard of polluted soils, contrary to the distribution of PAHs. The chemical analysis of water extracts of soil gave information on the soluble fraction corresponding to the pollutants directly accessible to organisms. Nevertheless, it was necessary to complete chemical analyses by eco-toxicity bioassays which proved to be more sensitive indicators of soil quality. The ecotox-score calculated from the selected battery of liquid and solid phase bioassays proved to be a robust method which allowed us to differentiate the two studied soils despite their similar total concentration of PAHs. In addition, the combination of chemical and toxicological approaches highlighted the relationship between acute ecotoxicity and 3-ring PAHs (most soluble compounds). In the same way, the chronic effect of both water extracts on algal growth can be explained by high molecular weight PAHs, such as 5- and 6-ring PAHs. As a conclusion, using ecotox-score can be a cost-effective assessment of PAHs polluted/remediated soils complementary to chemical analysis.

References

[1] Cerniglia, C.E., 1992. Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation*, **3**, 351-368.

[2] White, P.A., Claxton, L.D., 2004. Mutagens in contaminated soil: a review. *Mutation Research*; **567**, 227-345.

[3] Semple, K.T., Morriss, A.W.J., Paton, G.I., 2003. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. *European Journal of Soil Science*, **54**, 809-818.

[4] Chung, N., Alexander, M., 2002. Effect of soil properties on bioavailability and extractability of phenanthrene and atrazine sequestered in soil. *Chemosphere*, **48**, 109-115.

[5] Riding, M.J., Doick, K.J., Martin, F.L., Jones, K.C., Semple, K.T., 2013. Chemical measures of bioavailability/bioaccessibility of PAHs in soil: fundamentals to application. *Journal of Hazardous Materials*, **261**, 687-700.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas

ISBN: 978-960-6865-94-7

[6] Peijnenburg, W., Sneller, E., Sijm, D., Ljizen, J., Traas, T., Verbruggen, E., 2002. Implementation of bioavailability in standard setting and risk assessment. *Journal of Soils and Sediments*, **2**, 169-173.
[7] Lors, C., Ponge, J.F., Martínez Aldaya, M., 2010. Comparison of solid-phase bioassays and ecoscores to evaluate the toxicity of contaminated soils. *Environmental Pollution*, **158**, 2640-2647.
[8] Bispo, A., Jourdain, M.J., Jauzein, M., 1999. Toxicity and genotoxicity of industrial soils polluted by polycyclic aromatic hydrocarbons (PAHs*)*, *Organic Geochemistry Journal*, **30**, 947-952.
[9] Mendonça, E., Picado, A., 2002. Ecotoxocological monitoring of remediation in a coke oven soil, *Environmental Toxicol*ogy, **17**, 74-79.
[10] Eom, I.C., Rast, C., Veber, A.M., Vasseur, P., 2007. Ecotoxicity of a polycyclic aromatic hydrocarbon (PAH)-contaminated soil, *Ecotoxicology and Environmental Safety*, **67**, 190-205.
[11] Fent, K., 2003. Ecotoxicological problems associated with contaminated sites, *Toxicology Letters*, **140-141**, 353-365.
[12] Alexander, M., 1991. Research needs in bioremediation. *Environmental Sciences & Technology*, **25**, 1972-7973.
[13] Lors, C., Ponge, J.F., Martínez Aldaya, M., 2011. Comparison of solid and liquid-phase bioassays using ecoscores to assess contaminated soils. *Environmental Pollution*, **159**, 2974-2981.
[14] ISO 21268-2, 2007. Soil Quality - Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials. Part 2. Batch test using a liquid to solid ratio of 10 L/kg dry matter. International Organization for Standardization, Geneva.
[15] Verschueren, K., 2001. Handbook of Environmental Data on Organic Chemicals, fourth ed., Wiley, New York.
[16] ISO 13877, 1998. Soil Quality - Determination of polynuclear aromatic hydrocarbons, method using high-performance liquid chromatography. International Organization for Standardization, Geneva.
[17] ISO 11269-2, 2005. Soil Quality - Determination of the pollutants effects on soil flora. Part 2. Effects of chemicals on the emergence and growth of higher plants. International Organization for Standardization, Geneva.
[18] ISO 11267, 1999. Soil Quality - Inhibition of reproduction of Collembola (*Folsomia candida*) by soil pollutants. International Organization for Standardization, Geneva.
[19] Martínez Aldaya, M., Lors, C., Salmon, S., Ponge, J.P., 2006. Avoidance bio-assays may help to test the ecological significance of soil pollution. *Environmental Pollut*ion, **140**, 173-180.
[20] Lors, C., Martínez Aldaya, M., Salmon, S., Ponge, J.F., 2006. Use of an avoidance test for the assessment of microbial degradation of PAHs. *Soil Biology & Biochemistry*, **38**, 2199-2204.
[21] ISO 11348-3, 1998. Water Quality - Determination of inhibitory effects of water samples on the light emission of *Vibrio fischeri* (luminescent bacteria test). Part 3. Method with freeze-dried bacteria. International Organization for Standardization, Geneva.
[22] ISO 8692, 2004. Water Quality - Freshwater algal growth inhibition test with unicellular green algae. International Organization for Standardization, Geneva.
[23] Nesslany, F., Marzin, D., 1999. A micromethod for in vitro micronucleus assay. *Mutagenesis*, **14**, 403-410.
[24] Litchfield, J.T., Wilcoxon, F., 1949. A simplified method of evaluating dose-effect experiments. *Journal of Pharmacology and Experimental Therapeutics*, **96**, 99-113.
[25] Loibner, A.P., Szolar, O.H.J., Braun, R., Hirmann, D., 2004. Toxicity testing of 16 priority polycyclic aromatic hydrocarbons using Luminestox®. *Environmental Toxicology and Chemistry*, **23**, 557-564.
[26] Lors, C., Damidot, D., Ponge, J.F., Périé, F., 2012. Comparison of a bioremediation process of PAHs in a PAH-contaminated soil at field and laboratory scales. *Environmental Pollution*, **165**, 11.

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Determination of the toxicity of different environmental discharge waters using the acute toxicity tests approved for national pollutant discharge permit in Turkey

V. Zülal Sonmez[1,2], N. Sivri[1*], A. Handan Dökmeci[3]

[1] Department of Environmental Engineering, Istanbul University, Istanbul 34320, Turkey.
[2] Department of Environmental Engineering, Duzce University, Duzce 81620, Turkey.
[3] Department of Emergency and Disaster Management, Namik Kemal University, Tekirdag 59030, Turkey.
*Corresponding author: Email: sivrin@gmail.com

Abstract

Nowadays, three methods which target the evaluation of the characteristics of ecotoxicology tests according to aquatic trophic level, are well-known, approved methods. In Turkey, the toxicity dilution factor (TDF) method, approved by Turkish Water Pollution and Control Regulation, and *Lebistes reticulatus* the actual method name that utilizes this animal which is a high level consumer, are used in the assessment of acute toxicity levels of waste waters with different compositions. However; it is not preferred by researchers except statutory obligations due to its disadvantages in implementation. The other method *Daphnia magna*, which belongs to secondary trophic group, is also widely used. *Vibrio fischeri* which is based on bioluminescent bacteria is mostly preferred due to ability of giving fast and precise results in acute toxicity assessment tests. In this study, specific to Turkey, it is aimed to compare issues such as experimental process, time, cost, efficiency, repeatability, etc. of tests that take place in the related legislation and standards. In light of all this information, it is determined the insufficient parts about legal regulations related to toxicity in Turkey. It can be suggested that bioluminescence bacteria (*V. fischeri*), defined all around the world recently with its precision, optimal cost, repeatability features be used in Legal Regulations of Turkey. It is aimed to contribute to scientific literature, this study being the first on suggesting an innovative approach about acute toxicity test in Turkey.

Keywords: Microtox; heavy metals; interactive effect; bioavailability; toxicity; Turkish Water Pollution and Control Regulation

1. INTRODUCTION

Day by day, the more complex contaminants are, the bigger their effects on aquatic ecosystems become. Direct discharge of wastewater to receiving environment causes primary environmental effects such as forming toxic-carcinogenic aromatic amines under uncontrolled anaerobic conditions. It is insufficient to put forward this potential impact on living organisms in aquatic ecosystems by means of physical/chemical analysis [1]. The reason of this is that effluents having complex and toxic effects of usually unspecific contaminants and the potential synergistic or antagonistic effects among them can only be determined through toxicity tests [2]. Therefore, biological indicators have started to be used over time in order to determine the toxicity.

The application (implementation) on this subject, specific to Turkey, was first carried out by Şengül and Müezzinoğlu [3]. Şengül and Müezzinoğlu [3] applied toxicity test to fish at effluents of dyeing and paper industry, but could not observe any fish mortality for the dilution rates they applied [2]. Studies on ecotoxicological evaluation of industrial effluents [4] with simple and low cost toxicity test usage have accelerated over time. In recent years, the necessity of toxicity evaluation in industrial effluent discharge in Turkey has been mentioned by Sponza [5, 6], giving

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examples from different sectors such as paper, leather, petroleum chemicals, textile and metal industries. In these studies, acute toxicity was determined through bioassays at four trophic levels of bacteria (floc and coliform), algae (*Chlorella sp*.), protozoa (*Vorticella sp*.), and fish (*Lepistes sp*.). In other studies, it has been carried out acute toxicity of potassium permanganate [7] to fish bioassay, leather industry originated effluent to sea urchin (*P. lividus* and *S. granularis*), algae (*S. capricornutum*) [8], and textile industry originated effluent to *Daphnia magna* [9].

In this study, it is aimed to make a comparison on issues such as experimental process, time, cost, efficiency of test organisms taking place in the related regulations and standards specific to Turkey. Moreover, taking all industrial sectors into consideration, it is aimed to contribute to scientific literature with this study as the first to suggest innovative approaches to the related legislative regulations in Turkey.

2. ACUTE TOXICITY APPROACH IN TURKEY

Acute toxicity test was entered in force in Turkey with 'Water Pollution Control Regulation (WPCR) No. 25687 dated 04.09.1988 [10]. The term toxicity is based on a fish bioassay in determining acute toxicity in the related regulation. According to this regulation, toxicity is defined as 'to have the feature of leading to threaten human health, health of various indicator organisms, and the ecosystem balance; acute or chronic diseases, teratogenetic, genetic deformity and measurement (indication) by being within water in an amount more than a definite concentration' and TDF (toxicity dilution factor) is defined as 'measurement used to determine the toxicity level of effluents' [11]. It is used to determine the effect of toxicity on fish that are indicator organisms of effluent. The survival of fish in the end of 48 h, 72 h, and 96 h in different dilutions of effluent is determined through this experiment. It is a standard experiment providing the relationship of toxicity with dilution rates.

Fish bioassay is required from the industrial sector, like as food (TWPCR No: 5), mining (TWPCR No: 7), textile (TWPCR No: 10), petroleum (TWPCR No: 11), Vehicle Factories and Garages (TWPCR No: 18). Wastewater coming from industries such as textile, leather, chemicals is known to be potentially carcinogenic, and contain hazardous and toxic compounds. Effluents of these industries, having high chemical oxygen demand (COD) and suspended solids (SS), use excessive water and chemical substances at the same time. Besides the excessive water use, in mining, metal and petroleum industries have also heavy metal content having toxic effects. In the treatment of all these effluents, advanced oxidation process is needed except conventional treatment. If proper and sufficient treatment is not done, different chemical and heavy metal containing, and high volume effluents with high loads of organic substances will come out. These types of wastewaters may cause to the inhibition of performance on urban sewerage systems or secondary treatment units [12]. When taken into consideration that treatment will end in receiving environment, its effect on aquatic organisms is inevitable.

Although not included in Water Pollution Control Regulation, there are some toxicity test standards approved by Turkish Standards Institute (TSI) (Table 1). Among these, especially the freshwater type of Daphnia, *Daphnia magna*, is used as a test organism in water quality control, and studies as well as on the determination of the toxicity of wastewater and/or chemicals.

Acute toxicity tests carried out with *Daphnia magna* have taken place in academic studies very often [14-16]. This organism is used due to its rapid growth rate, high spawning potential, short life cycle and having indicator features [17]. Studies are carried out on different test organisms about effluent toxicity within the scope of SCI. In studies carried out between 2003 and 2015 in Turkey, acute toxicity tests using *Daphnia magna* attract most attention. Another one acute toxicity tests known as Resazurin method [18, 19] carried out using bacteria. Although not preferred by scientists, fish bioassay is also one of the most widely used tests due to its presence in official regulations.

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Table 1: Toxicity Test Standards approved by Turkish Standards Institute (TSI) [13].

DATE	TS NO	STANDARD NAME
4.4.1988	TS 5676	Water Pollution Control-Toxicity Tests
5.4.1990	TS 8264	Industrial Effluents and Wastewaters-Acute Toxicity Tests-Bioassay Methods
14.4.1997	TS EN ISO 10712	Water quality-*Pseudomonas putida* growth inhibition test (Pseudomonas cell multiplication inhibition test)
18.9.1997	TS 11981 ISO/DIS 14669	Water quality-Cruslaces bioassays- Determination of acute lethal toxicity to marine copepods (Copepode, Crustacea)
30.12.1997	TS ISO 10229	Water quality-Determination of the prolanged toxicity of substances to freshwater froh method for evaluating the effects of substances on the growth rate of the rainbow trout
12.4.2000	TS 6020 EN ISO 7346	Water quality- Determination of the acute lethal toxicity of substances to a freshwater fish [*Brachydonio Rerio Hamilton-Buchanan* (*Teleostei, Cyprinidae*)]
17.3.2005	TS ISO 10706	Water Quality- Determination of Long Term Toxicity of Substances to *Daphnia magna straus* (Cladocera, Crustacea)
12.10.2006	TS EN ISO 10253	Water quality - Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*
12.10.2006	TS EN ISO 9509	Water quality - Toxicity test for assessing the inhibition of nitrification of activated sludge microorganisms
27.3.2007	TS EN ISO 16712	Water quality - Determination of acute toxicity of marine or estuarine sediment to amphipods
27.3.2007	TS EN ISO 20079	Water quality - Determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*) - Duckweed growth inhibition test
19.1.2010	TS EN ISO 15088	Water quality - Determination of the acute toxicity of waste water to zebrafish eggs (*Danio rerio*)
19.1.2010	TS EN ISO 11348	Water quality - Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test)
10.4.2013	TS EN ISO 6341	Water quality - Determination of the inhibition of the mobility of *Daphnia magna straus* (Cladocera, Crustacea) - Acute toxicity test
12.6.2013	TS EN ISO 10710	Water quality - Growth inhibition test with the marine and brackish water macroalga *Ceramium tenuicorne*

3. CONCLUSIONS

The results of toxicity test indicate the potential hazard to the aquatic ecosystem. It is necessary to make the risk evaluation of toxicants based on national/international regulations in order to be able to evaluate the results of the tests. Thus, it is possible to keep the chemicals that may occur in the environment within the frame of Acceptable Risk Level (ARL). Even if sectors determined in the related regulation do not exceed the limits of effluent discharge, they may cause toxicity. However, effluent investigated for its Toxicity Dilution Factor (TDF) does not indicate its toxicity completely. The most important insufficiency of Toxicity Dilution Factor is that it does not measure the reaction

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of organisms while indicating toxicity. As Aydın and Kara [2] mentioned in their studies, although 30 times diluted effluent does not cause fish death, it is impossible to predict the real effect of it or how it reacts when diluted 10 times. Therefore, LC_{50} is preferred to TDF in tests of fish bioassays carried out in Turkey by researchers.

It has been tried to determine hazards that may occur in aquatic ecosystem by using more than one organism in many studies. Due to these organisms at different trophic levels showing different sensitivity, a number of series of test application is needed. Nevertheless, feasibility of bioassays carried out with more than one organism is low due to its time and cost factors. The reason of failure of fish bioassays is this infeasibility. What really matters is finding the most precise, the most appropriate, and the most accurate method. In the selection of the suitable test organism, with its representing the ecosystem, easy organism supply/preservation feature, wide range of sensitivity, high adaptation capacity, and being less affected by environmental parameters, the type of test organism becomes more advantageous. Due to this reason, test organisms categorized according to their trophic levels given in Table 3 should be investigated with their advantages and disadvantages. It can be recommended to use bioluminescent bacteria (*V. fischeri*), being recently defined worldwide with its sensitivity, optimal cost, and repeatability, in Turkish Legislative Regulations. In developed countries such as the USA, Germany, France, and Spain, this test has been approved to be the prominent acute toxicity test accepted as an official standard.

Table 3: Advantages and disadvantages of acute toxicity organisms which are mostly used in Turkey (adapted from Karci [20]).

TEST ORGANISM	ADVANTAGE	DISADVANTAGE
Microorganisms	• Representing organisms at higher trophic levels • More precision compared to invertebrates and fish • Repeatability of tests • Resulting in 30 minutes rather than days/hours • More optimal cost • More ethical because it does not harm higher structured organisms • Storage of reagent/ auxiliary chemicals for about 1 year • Being appropriate for all air, surface and underground water, effluent, sediment, and chemical samples • No need for ventilation even in samples of effluents/underground waters with low level DO • Working on small sample volumes in millilitres • No need to prepare cultures due to freeze dried reagents(optional) • No possibility of being exposed to different toxicants throughout their lifecycle and low possibility of adaptation • The real reason of death being highly toxicant based • No need for specialisation	• Possibility of the sample losing its own feature due to special sample preparation (solvent, salinity, pH adjustment, etc.)
Invertebrates	• Being types having economical or ecological importance • Being small-sized, and having a short lifecycle • Getting genetically uniform cultures, standardised stock organism	• Lack of information in methods of cultures many types • Possibility in being exposed to the former toxicant during lifetime • Difficulty in knowing real reason of death

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Table 3 (continued)

Fish	• Understandable toxicant intake, behaviour, and reactions • Appropriate for monitoring pollution in aquatic systems • Good precision, realtime analysis	• Different reaction of different types due to physiological differences • Long lasting test • Standardisation problems • High amount of sample volume • Difficulty in knowing real reason of death • Being affected by environmental parameters • Possibility in being exposed to the former toxicant during lifetime, giving different reactions

4. DISCUSSION

Toxicity on which there are many studies carried out worldwide, by analysing the legislative regulations especially in Turkey it can be seen that it is not at a sufficient level. While the last revision of Water Pollution and Control Regulation was done on 24.04.2011, it has not been revised since the addition of toxicity tests into the regulation. In the Turkish Regulation, fish bioassay and toxicity dilution factor is the only toxicity monitoring parameter for the permission of effluent discharge. The insufficiency determined in the related regulation can be stated as gaps in legislative regulations, way of practice, and insufficiency of test organisms used in acute toxicity tests.

Many of the acute toxicity tests used by Turkish Standards Institute are in English language. Furthermore many standards have not been translated into Turkish, however, they should be translated into the first language in order to enable those who are interested in this subject to have a more active role in these studies.

In Turkey, where industrialisation is increasing constantly, discharge of effluent of both the difficult ones to treat and the ones where more than one type of effluent is mixed, is done after conventional treatment. This causes the toxicant to increase its pressure on the recipient environment, and the xenobiotics to enter the environment easily. According to Water Pollution Control Regulation, with the statement “If found necessary by the related authority, Fish Bioassay is checked in investigations” the only parameter that reveals the effect of toxicants on ecosystems may be eliminated.

Environment issues have gained importance in Turkey together with the improvements worldwide. Especially in the frame of the EU membership negotiations, Turkey should develop and update its legislative regulations on water resources. Having approximately 100 laws and regulations, and many organizations and institutions in the management of water resources being effective in the issue in our country causes some complications. When our legislative regulations are evaluated in terms of acute toxicity, primarily there should be different organisms and laboratory studies including protocol use for the evaluation of toxicity. The aim of these studies should be obtaining sufficient information on acute toxicity with bioluminescent bacteria that is an appropriate bioassay, having the advantage of superseding fish bioassays due to its being more ethical for animal welfare, being easy, highly precise, and relatively cheap. As an untouched issue, acute toxicity tests should be brought into question by organisations and institutions cooperating with universities. Thus, it is foreseen that following the developed countries, improvements in acute toxicity determination may occur.

ISBN: 978-960-6865-94-7

References

[1] Villegas-Navarro., A, González, M. R., Lopez, E.R., Aguilar, R.D. and Marcal, W.S., 1999. Evaluation of *Daphnia magna* as an Indicator of Toxicity and Treatment Efficacy of Textile Wastewaters. *Environment International*, **25(5)**, 619-624.doi:10.1016/S0160-4120(99)00034-3.

[2] Aydın, M.E. and Kara, G., 2006. Toxicity of Organizated Industrial Zone Wastewater. *Journal of the Faculty of Engineering and Architecture of Selcuk University,* **21 (3-4)**, 13-20.

[3] Şengül, F. and Müezzinoğlu, A., 1987. Atıksularda Balık Biyodeneyinin Uygulanması ve ZSF Hesabı ile İlgili Bir Örnek Çalışma. MSc diss., Dokuz Eylül University. (in Turkish)

[4] Aydın, M.E., Aydin, S., Tongur, S., Kara, G., Kolb, M., Bahadir, M., 2015. Application of Simple and Low-Cost Toxicity Tests for Ecotoxicological Assessment of Industrial Wastewaters. *Environmental Technology,* **36 (22)**, 1-34. doi:10.1080/09593330.2015.1049216.

[5] Sponza, D.T., 2002. Incorporation of Toxicity Tests into the Turkish Industrial Discharge Monitoring Systems. *Archives of Environmental Contamination and Toxicology* **43(2)**, 186-197. doi: 10.1007/s00244-002-1150-2.

[6] Sponza, D.T., 2002. Necessity of Toxicity Assessment in Turkish Industrial Discharges (Examples from Metal and Textile Industry Effluents). *Environmental Monitoring and Assessment*, **73(1)**, 41-66.

[7] Aslantürk, A. and Çetinkaya, O., 2014. Acute Toxicity of Potassium Permanganate ($KMnO_4$) on Guppy (*Poecilia reticulata*, Peters, 1859). *Süleyman Demirel Üniversitesi Eğirdir Su Ürünleri Fakültesi Dergisi,* **10 (1)**, 12-19. (in Turkish).

[8] Oral, R., Meriç, S., Nicola, E. D., Petruzzelli, D., Rocca, C. D. and Pagano, G., 2007. Multi-Species Toxicity Evaluation of a Chromium-Based Leather Tannery Wastewater. *Desalination,* **211 (1)**, 48-57.

[9] Meriç, S., Selçuk, H. and Belgiorno, V., 2005. Acute Toxicity Removal in Textile Finishing Wastewater by Fenton's Oxidation, Ozone and Coagulation–Flocculation Processes. *Water Research,* **39 (6)**, 1147-1153. doi:10.1016/j.watres.2004.12.021.

[10] TWPCR, Turkish Water Pollution Control Regulation (1988) Official Gazette No. 19919, 4 September.

[11] Bahadır, E. B. and Meriç Pagano, S., 2013. Statistical Correlation of Toxicity Monitoring Method with Pollution Parameters for Industrial Wastewater Discharges in Turkey. Nigde *University Faculty of Engineering and Architecture Journal of Engineering Sciences,* **2 (2)**, 1-8. (in Turkish).

[12] Birgül, A. and Solmaz, S. K. A., 2007. Investigation of COD and Colour Removal on a Textile Industry Wastewater Using Advanced Oxidation and Chemical Treatment Processes. *Ecology* **15 (62)**, 72-80. (in Turkish).

[13] URL 1: Turkish Standards Institution (TSI). https://www.tse.org.tr/tr/Default.aspx (acessed on: December 2015).

[14] Meriç, S., Kaptan, D. and Ölmez, T., 2004. Color and COD Removal from Wastewater Containing Reactive Black 5 Using Fenton's Oxidation Process. *Chemosphere,* **54 (3)**, 435-441. doi:10.1016/j.chemosphere.2003.08.010.

[15] Arslan-Alaton, I., 2007. Degradation of a Commercial Textile Biocide with Advanced Oxidation Processes and Ozone. *Journal of Environmental Management*, **82 (2)**, 145-154. doi:10.1016/j.jenvman.2005.12.021.

[16] Sponza, D. T. and Kuscu, Ö. S., 2011. Relationships between Acute Toxicities of Para Nitrophenol (P-NP) and Nitrobenzene (NB) to *Daphnia magna* and *Photobacterium phosphoreum*: Physicochemical Properties and Metabolites under Anaerobic/Aerobic Sequentials. *Journal of Hazardous Materials,* **185 (2)**, 1187-1197. doi:10.1016/j.jhazmat.2010.10.030.

[17] Sarı, E., 2011, Investigation of Acute Toxicity of Nickel to *Daphnia magna* (straus,1820)(Crustacea:Cladocera). MSc diss., Ankara University. (in Turkish).

[18] Kargi, F., and Konya, I., 2006. COD, Para-Chlorophenol and Toxicity Removal from Para-Chlorophenol Containing Synthetic Wastewater in an Activated Sludge Unit. *Journal of Hazardous Materials,* **132 (2)**, 226-231. doi:10.1016/j.jhazmat.2005.09.040.

[19] Eker, S. and Kargi, F., 2006. Kinetic Modeling and Parameter Estimation in Biological Treatment of 2, 4-Dichlorophenol Containing Wastewater Using Rotating Perforated Tubes Biofilm Reactor. *Enzyme and Microbial Technology,* **38 (6)**, 860-866. doi:10.1016/j.enzmictec.2006.01.012.

[20] Karci, A., 2014. Degradation of Chlorophenols and Alkylphenol Ethoxylates, Two Representative Textile Chemicals, in Water by Advanced Oxidation Processes: The State of The Art on Transformation Products and Toxicity. *Chemosphere,* **99**, 1-18. doi:10.1016/j.chemosphere.2013.10.034.

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Cumulative impacts from multiple human activities on *Posidonia oceanica* seabeds in eastern Mediterranean waters

M. M. Brodersen[1], A. Kokkali[1], E. Kaberi[2], M. Pantazi[1], I. Maina[1], S. Kavadas[1], P. Panayotidis[2], V. Gerakaris[2], V. Vassilopoulou[1*]

[1] Institute of Marine Biological Resources and Inland Waters, Hellenic Centre for Marine Research, PO BOX 712, 19013, Anavyssos, Greece.
[2] Institute of Oceanography, Hellenic Centre for Marine Research, PO BOX 712, 19013, Anavyssos, Greece.
*Corresponding author: Email: celia@hcmr.gr

Abstract

A strategy for achieving sustainable delivery of ecosystem services is Ecosystem-Based Management (EBM) that addresses the fundamental need to account for cumulative impacts of human activities. Saronikos Gulf belongs to the Aegean Sea and provides a wide range of ecosystem services, however, the status of certain marine ecosystem components seems to be affected by multiple human activities. The aim of this study is to assess the cumulative impacts from land-based activities, port infrastructures, aquaculture and small scale fisheries on the *Posidonia oceanica* meadows in the Saronikos Gulf and was conducted under the SEAS-ERA MERMAID project. The methodology proposed by Halpern *et al*. (2007, 2008) as modified by Korpinen *et al*. (2012) was used, taking into account the vulnerability of this habitat to each of the stressors using expert judgement (Halpern *et al*., 2007). The main results indicated that the most impacted areas of the *P.oceanica* meadows are in the inner part of the Gulf, adjacent to the most urbanised coastal areas of the Prefecture of Attiki and near port infrastructures. Land-based pollution as well as siltation and abrasion of the sea bottom due to shipping and docking activities seem to be the main pressures on the meadows. Understanding cumulative impacts is crucial for informing policy decisions under an EBM approach.

Keywords: vulnerability; ecosystem component; seagrass; Aegean Sea.

1. INTRODUCTION

Increasing pressure on the marine environment due to human activities has led the European Union (EU) to adopt the Marine Strategy Framework Directive (MSFD) aiming at the "Good Environmental Status" (GES) of EU waters by 2020. The Saronikos Gulf, located in the oligotrophic South Aegean Sea, receives the effluents of the city of Athens and is also subjected to a number of pressures from the human activities exerted in the area. These pressures seem to have impacts on the Saronikos ecosystem [1] and particularly on certain conservation priority habitats, such as the *P. oceanica* (sea grass) meadows [2]. *P. oceanica* is included in the list of strategic habitats for the conservation of biodiversity within the EC Habitats Directive. In this study, conducted in the frame of the SEAS-ERA MERMAID project, cumulative impact assessment was applied on areas of the Saronikos where *P. oceanica* meadows exist [3]. These areas are subjected to pressures from different human activities, such as small scale fisheries, aquaculture, coastal infrastructures, land-based activities, particularly from Athens, the most densely populated city, and Piraeus, the busiest port in Greece. This study aims to shed light on areas subjected to high pressures which may lead to the degradation of the ecological status of key ecosystem components and emphasizes the need for comprehensive monitoring and application of cumulative impacts assessment as the basis for implementing effective spatial management plans.

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2. MATERIALS AND METHODS

2.1 Description of the case study area

The Saronikos Gulf is situated at the South Aegean Sea (northeast Mediterranean) surrounded by the peninsulas of Attica at the north and the NE Peloponnese at the south. There are several islands and islets in the Gulf, Salamina and Aegina being the most important in terms of size and population density. The length of the coastline is ~ 270km, the surface ~ 2.866km^2 and the mean water depth is ~100m. The Gulf is subjected to intense anthropogenic pressures as it is the marine border of the cities of Athens with ~5 million inhabitants [4] and Piraeus. Along its northern coast (~135km) there are numerous industrial activities including the industrial zone of Athens in the Elefsis embayment and Piraeus port, one of the largest in the Mediterranean. In addition the gulf receives the treated wastewaters of the aforementioned cities as well as of smaller towns and settlements. Two small urbanized rivers (Kifissos and Ilissos), have low base flow due to boxing and burial beneath major street arteries and urban development. Several point and non-point pollution sources are present in the greater area of the Saronikos Gulf and Elefsis Bay. One of the most important point sources is the Athens wastewater treatment plant (WWTP) which is situated on the small island of Psittalia and discharges 750000 t d^{-1} [5] treated wastes (secondary treatment since 2004) into the inner Saronikos Gulf (ISG) at ~65m depth. Other point sources are spread along the coasts and include marinas, touristic facilities and fish farms, while non-point pollution sources for the Saronikos Gulf include marine traffic, and possibly the atmospheric deposition of pollutants from the adjacent urban areas. Other human activities affecting the ecosystem are the extensive modification of the coastline and the overfishing. Most activities have direct input to the Gulf's waters while others contaminate the soils or the groundwater affecting the marine environment via runoff and/or SGDs. Moreover, it is subjected to an unprecedented introduction of alien species, largely due to the area's intense maritime traffic and the Lessepsian (i.e. through the Suez Canal) immigration phenomenon, which has been strongly affecting the wider Eastern Mediterranean basin during the last two decades [6], impacting mainly small scale fishery catches of the Saronikos [7]. The human activities used for the analysis are illustrated in Figure 1.

P. oceanica meadows are mainly distriduted in the Inner and Outer part of Saronikos Gulf while they are absent in the Western part. *P. oceanica* meadows are among the most important coastal habitats in the Mediterranean and as an ecological climax they provide major benefits [8].The spatial distribution of *P. oceanica* is presented in Figure 2.

2.2 Methodology

In this study, conducted in the frame of the SEAS-ERA MERMAID project, cumulative impact assessment was applied to identify areas of *P. oceanica* which appear to be under high pressure from key human activities/uses. The analysis was based on the assessment of five vulnerability measures, proposed by Halpern *et al.* [9,10] and modified by Korpinen *et al.* [11], for the specific ecosystem component using expert judgment. At first, experts identified which of the human activities taken place in the areas of *P. oceanica* distribution could affect this habitat. These activities include small scale fisheries, aquaculture, land-based activities (agriculture, industry, urbanization) and coastal defence infrastructures. Spatial data related to human activities/uses in the area were used in two ways either with presence/absence data for aquaculture [12], and coastal defence infrastructures [13], or indices for small scale fisheries [14] and land based activities [15]. The estimation of fishing pressure index from small scale fisheries was based on Multi Criteria Decision Analysis (MCDA) methodology which used influential components affecting coastal fishing [14]. Land Use Simplified Index (LUSI) illustrates the degree of impacts that land use

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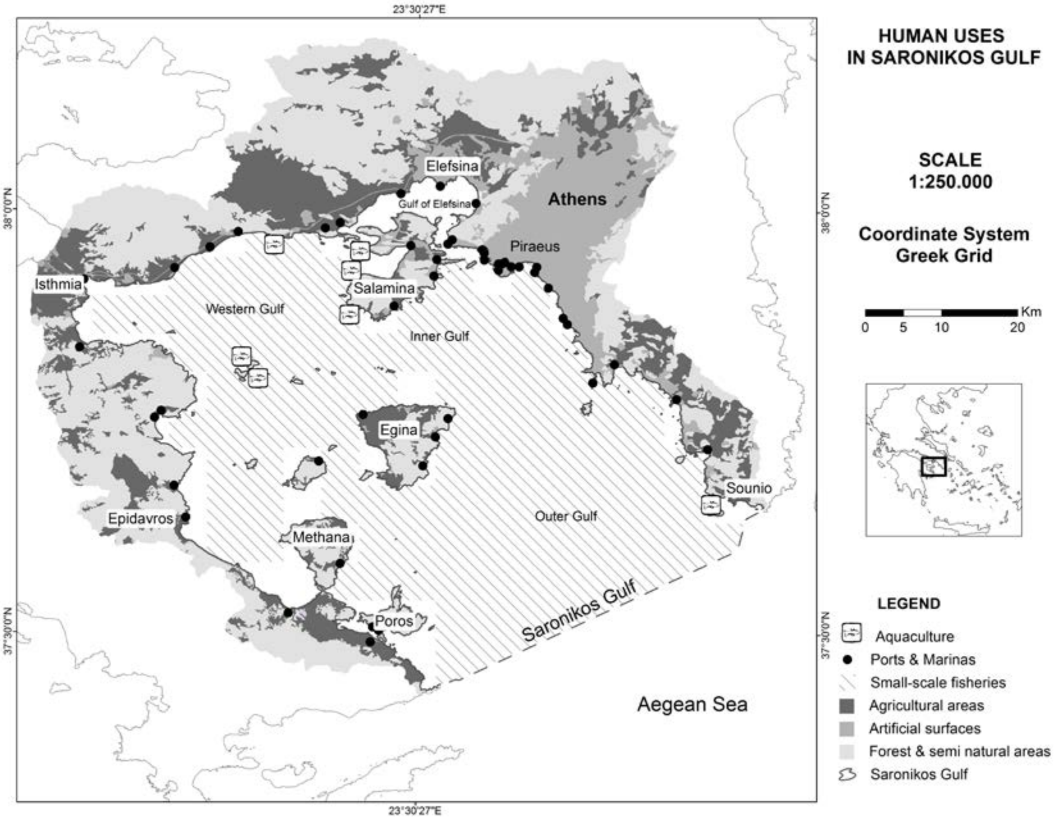


Figure 1. Human activities/uses in Saronikos Gulf (Source: HCMR).

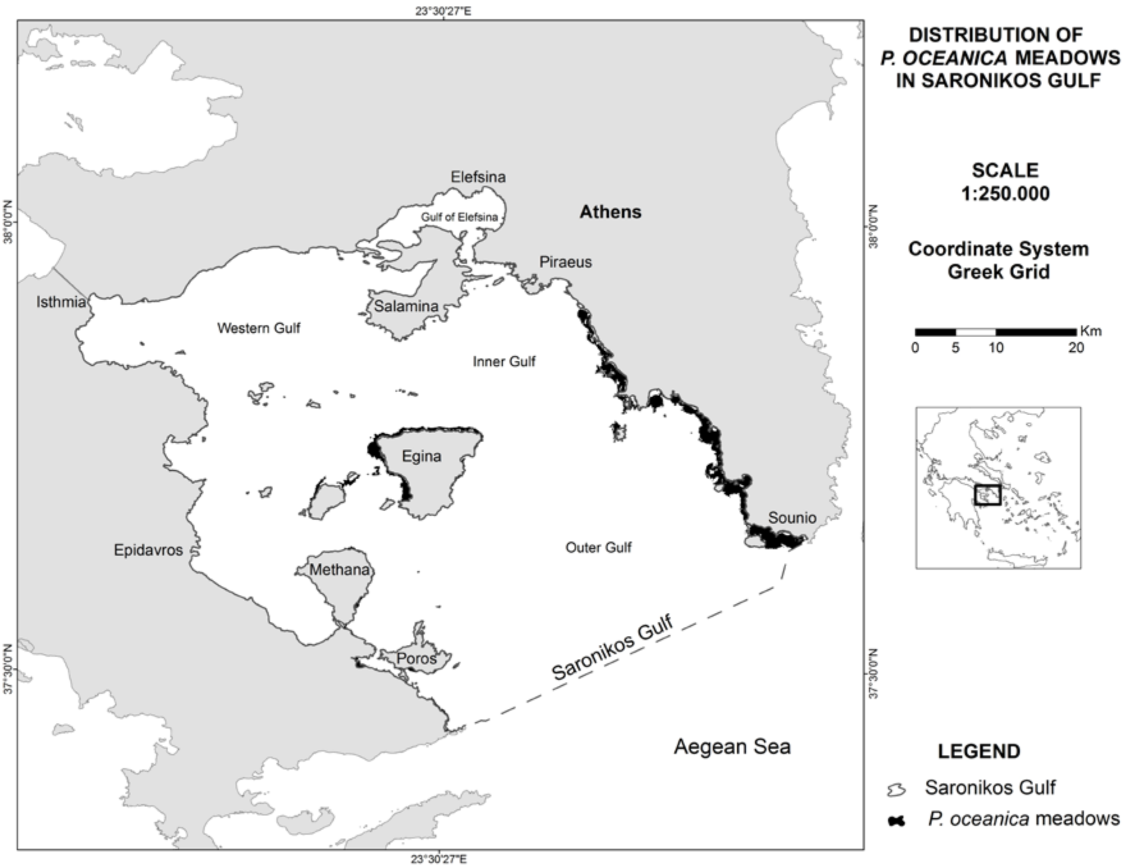


Figure 2. Spatial distribution of *P. oceanica* meadows in Saronikos Gulf (Source: HCMR).

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activities (agriculture, urbanization, industry) exert on each water body. The application of the LUSI index in the Hellenic coastal waters was based on Corine Land Cover 2000 data, using specific GIS software [15]. Data referring to the distribution of the habitat under study were derived from Panayotidis *et al.* [2]. The results provided cumulative impact scores of combined human activities into 1km^2 pixel of *P. oceanica* distribution area. The calculated cumulative human impacts on *P. oceanica* were mapped in ArcGIS 10 environment.

3. RESULTS

Following the aforementioned methodology, vulnerability scores were assessed according to which higher cumulative impacts occurred in the inner Saronikos Gulf and seemed to be connected with land based activities and coastal infrastructures (Figure 3). Outcomes indicate the areas where the specific ecosystem component seems to be under greater pressure.

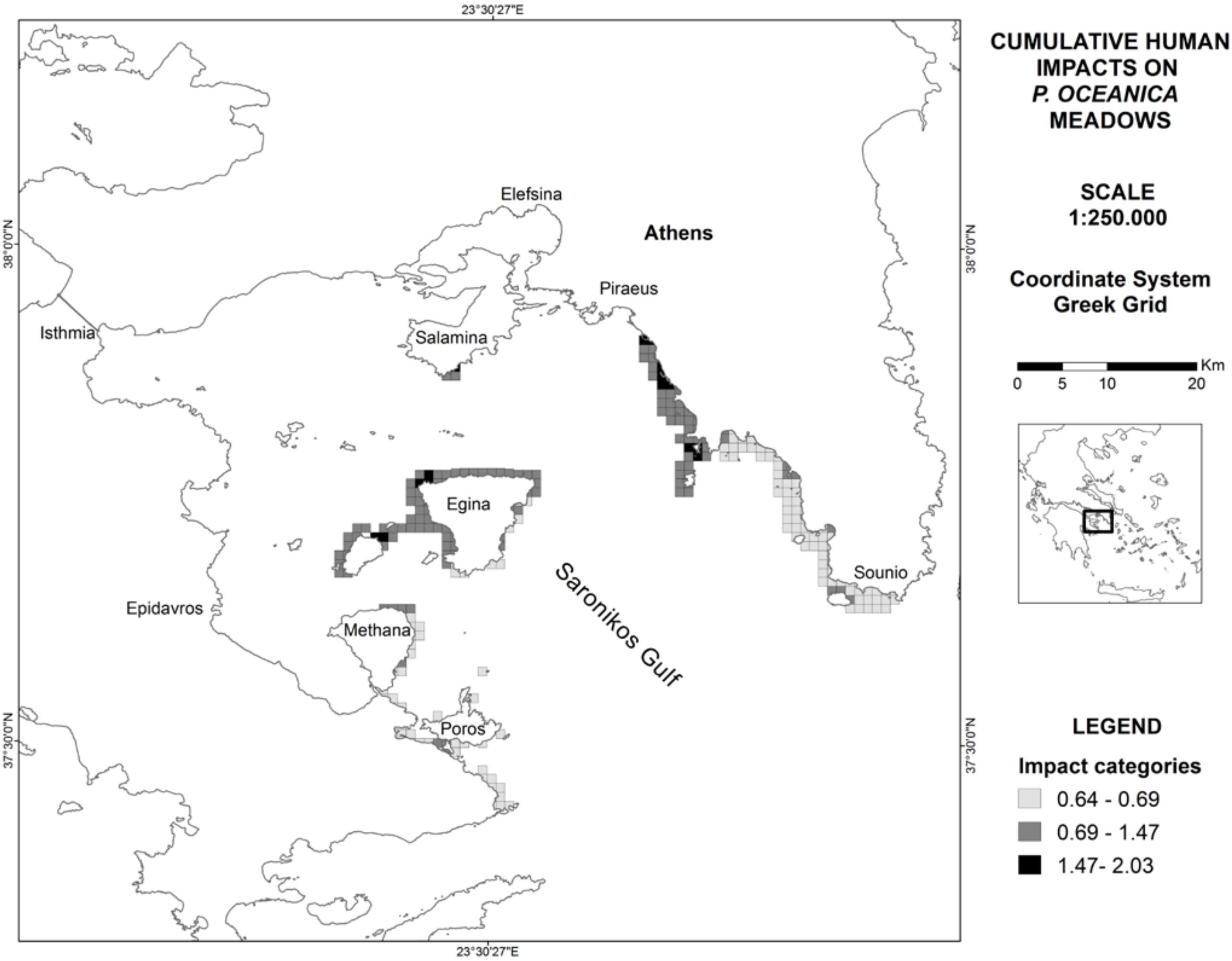


Figure 3. Spatial distribution of cumulative human impacts on *P. oceanica* meadows across Saronikos Gulf. Color scales correspond to the impact categories listed in the legend (Source: HCMR).

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4. DISCUSSION/ CONCLUSIONS

This study identified areas that are under significant pressure exerted by existing human activities. *P. oceanica* meadows in the Inner Saronikos are subjected to higher pressures due to the high concentration of coastal infrastructures and the effluents received from the Athens metropolitan area. Although there are no significant differences in the distribution pattern of *P. oceanica* in the last 30 years [16,2], important human pressures continue to be exerted which could lead to the degradation/loss of the specific habitat in these areas.

According to the results of this study, the *P. oceanica* meadows of the outer part of Saronikos Gulf are not as impacted as in the Inner part. However, the coexistence of significant activities such as aquaculture and increase in sedimentation rates in the inner Saronikos Gulf highlights the importance of further protection and monitoring of the area, as meta-analysis conducted by Claudet & Frascetti [17] has shown that the above stressors constitute major threats for these meadows [18] which can lead to high mortality rates and negative effects on phanerogam's morphological variables.

The establishment of effective spatial management plans aiming to mitigate impacts of human activities is of paramount importance contributing to the achievement of GES in the area under study and constitutes a good example of integration between the goals of the MSFD and the MSP Directive.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Tornero, V., D'Alcalà, M.R., Buia, M.C., Arashkevich, E., 2013. PERSEUS D2.1: Pressures and their impacts on coastal ecosystems in the SES, Gap Analysis - Preliminary report.

[2] Panayotidis P., Gana S., Karamfilov V., Zouljevic A., Micu D., Buia, M.C., 2015. PERSEUS D2.6: Response of benthic ecosystems under the influence of coastal pressures in different sub-regions of the South European Seas (SES). PERSEUS IP project.

[3] Panayotidis, P., Karamfilov, V., Berov, D., Hiebaum, G., Klayn, S., Gerakaris, V., Lardi, P., 2014. Seagrass presence and distribution as Ecological Status Indicators: Case studies in the Eastern Mediterranean and the Black Sea. In: 2nd Scientific Workshop of PERSEUS, December, Marakesh, Morocco.

[4] Pavlidou A., Kapari M., 2010. Nutrients in transitional, coastal and marine waters. *Report of streamlining European biodiversity indicators, Vol 15*. Hellenic Centre for Marine Research, Athens, 8.

[5] Ξενάριος Σ., 2009. Αξιολόγηση των άμεσων ωφελειών στους υδατικούς αποδέκτες αστικών συστημάτων αποχέτευσης. Διδακτορική Διατριβή, Πάντειον Πανεπιστήμιο, Αθήνα.

[6] Tsiamis K., Montesanto B., Panayotidis P., Katsaros C., Verlaque M., 2010. Updated records and range expansion of alien marine macrophytes in Greece. *Mediterranean Marine Science*, 11, 61−79.

[7] Brodersen, M.M., Chalari, N., Diktyopoulos, C., Dogrammatzi, A., Vassilopoulou, V., 2016. Preliminary comparative study of trammel net fisheries in the Saronikos Gulf, 2016. *Proceedings of the 16th Pan-Hellenic Conference of Ichthyologists*, October 6-9, Kavala, Greece (to be presented).

[8] Duarte, C.M., 1991. Allometric scaling of seagrass form and productivity. *Marine Ecology Progress Series*, 77, 289–300.

[9] Halpern, B.S., Selkoe, K.A., Micheli, F., Kappel, C.V., 2007. Evaluating and ranking the vulnerability of global marine ecosystems to anthropogenic threats. *Conservation Biology*, 21, 1301–1315.

[10] Halpern, B.S., Walbridge, S., Selkoe, K.A., Kappel, C.V., Micheli, F., D'Agrosa, C, *et al*. 2008. A Global Map of Human Impact on Marine Ecosystems. *Science*, 319, 948–952.

[11] Korpinen, S., Meski, L., Andersen, J.H., Laamanen, M., 2012. Human pressures and their potential impact on the Baltic Sea ecosystem. *Ecological Indicators*, 15, 105-114.

[12] Υπουργείο Περιβάλλοντος, Χωροταξίας και Δημοσίων Έργων. Γενική Διεύθυνση Περιβάλλοντος, Διεύθυνση Χωροταξίας, 2000. Στρατηγικό πλαίσιο κατευθύνσεων για την ανάπτυξη των θαλάσσιων υδατοκαλλιεργειών στην Ελλάδα.

[13] Kavadas, S., Damalas, D., Georgakarakos, S., Maravelias, C., Tserpes, G. *et al*., 2013. IMAS-Fish: Integrated Management System to support the sustainability of Greek Fisheries resources. A multidisciplinary webbased database management system: implementation, capabilities, utilization & future prospects for fisheries stakeholder. *Mediterranean Marine Science*, 14(1), 109-118.
[14] Kavadas, S., Maina, I., Damalas, D., Dokos, I., Pantazi, M., Vassilopoulou, V., 2015. Multi-Criteria Decision Analysis as a tool to extract fishing footprints: application to small scale fisheries and implications for management in the context of the Maritime Spatial Planning Directive. *Mediterranean Marine Science*, 16 (2), 294-304.
[15] Lampou, A., Simboura, N., Drakopoulou, P., Panayotidis, P., 2015. Application of the Land Use Simplified Index (LUSI) in the Hellenic coastal waters (Eastern Mediterranean) and cross-correlation with their Integrative Environmental Status. *Proceedings of the 11th Panhellenic Symposium on Oceanography and Fisheries* (eds. Karachle, P.K., Giannakourou, A., Zervoudaki, S. *et al*.), Mytilene 13-17 May, Lesvos island, Greece, 729-732.
[16] Panayotidis, P., Simboura N., 1985. Distribution and phenology of *Posidonia oceanica* in Saronicos Gulf (Aegean Sea, Greece). *Proceeding of the 2nd International Workshop on Posidonia beds*, GIS Posidonie, 43-48.
[17] Claudet, J., Frascetti, S., 2010. Human-driven impacts on marine habitats: A regional meta-analysis in the Mediterranean Sea. *Biological Conservation*, 143, 2195–2206.
[18] Díaz-Almela, E., Marbà, N., Álvarez, E., Santiago, R., Holmer, M. *et al*., 2008. Benthic input rates predict seagrass (*Posidonia oceanica*) fish farm-induced decline. *Marine Pollution Bulletin*, 56, 1332–1342.

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Bioaccumulation of cobalt and nickel in macrophytes from Skadar Lake

V. Kastratović[1], M. R. Bigovic[1*], Ž. Jaćimović[2], M. Kosović[2], D. Đurović[3], S. Krivokapić[1]

[1] Faculty of natural sciences and mathematics-Department of biology-University of Montenegro, Podgorica, Montenegro.
[2] University of Montenegro, Faculty of Metallurgy and Technology, Montenegro.
[3] Institute of Public Health of Montenegro, Podgorica, Montenegro.
*Corresponding author: Email: mbigovicnk@gmail.com

Abstract

Macrophytes react to changes in the quality of the environment in which they live (water/sediment), and they are good bioindicators of surface water condition. In the present study, the content of metals Co and Ni were determined in the sediment, water and different organs of macrophytes from six localities around Lake Skadar, in four different seasons of year. Aquatic macrophytes that have been used as bioindicator species in this study are *Phragmites australis* (emerged), *Ceratophyllum demersum* (submerged) and *Lemna minor* (floating). The aim of this study was determining the distribution of metals in macrophyte tissues and also to discover the degree of bioaccumulation of the investigated metals, depending both on location and season. Content of Co and Ni in the examined parts of macrophytes were in the range of 0.11-3.88 mg kg^{-1} and 1.74-15.6 mg kg^{-1} respectively. The concentration of investigated metals decreases in the following order: *C. demersum* > *L. minor* > *P. australis*. The highest contents of the investigated metal in the organs of *P. australis* and *C. demersum* were recorded in the beginning and during the growing season. Higher concentrations of metals in the tissue of *L. minor* were observed at the end of the growing season.

Keywords: Skadar Lake; macrophytes; cobalt; nickel; bioindicator

1. INTRODUCTION

The rapid evolvent of industrialization and urbanization has led to the pollution of ecosystems by heavy metals. Heavy metals are one of the most important and potentially toxic group of chemical substances, which may be present in the aqueous medium. Their origin is from natural and anthropogenic sources. Natural waters, especially fresh water systems, besides their polluting in varying degrees, they are also convicted to a fairly long-term pollution by metals in sediments deposited since the early human activity from the Middle Ages [1]. Macrophytes have an inevitable role in the overall functioning of the lake. They are also important components of aquatic systems because they perform sorption of harmful substances, causes their decomposition and filtration. Besided, macrophytes are efficient accumulators of heavy metals [2]. Abilities of water plants to accumulate heavy metals are increasingly used to monitor changes arising from environmental pollution [3]. An important role of aquatic flora stems from the fact that in the macrophyte tissue metal concentrations can be 10^5 times higher than in the surrounding water [4]. Depending on the species, in tissue of macrophytes metals can be present in the quantity of the order or greater than those in the nearby sediment [5], and often up to a thousand times higher than the necessary amount of metal unimpeded growth and development of plants.

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Unlike water and sediments, in plants was observed significant changes in the concentration of metals depending on the weather. For phyto-management, it is necessary to take into consideration seasonal changes of metal concentration in plants[6-8].

The main purpose of this study was to determine the distribution of metals adopted in some parts of macrophytes and differences and degree of bioaccumulation of cobalt and nickel, depending on the test plants, their location and season.

2. MATERIALS AND METHODS

The aquatic macrophytes which are used as indicator species in this study are: *Phragmites australis*, *Ceratophyllum demersum* and *Lemna minor* taken from six locations around Lake Skadar, Montenegro. The locations are: the left and right estuary of the Moraca River, Rijeka Crnojevica, Plavnica, Radus and Crni Zar. The samples were collected during four separate periods in 2011. The samples of *P. australis* and *C. demersum* were collected four times during 2011 at six locations. The samples of *L. minor* were collected in two time periods, in August and October, from four locations. Samples of sediment and water were taken at the same time and from the same places as where the plant material was taken.

The plant material was separated in the laboratory into the root, stem and leaf of *P. australis*, the stem and leaf of *C. demersum* and the root and leaf of *L. minor* with the intention of determining the bioaccumulation of the plant in each organ. The plant material then was dried at 75^{o}C over a 48 hour period. The samples were grinded to a fine powder and homogenized. The samples were mineralized to avoid the influence of the matrix. The prepared plant samples were mineralized in a Milestone Microwave Ethos 1, with a mixture of HNO_3 and H_2O_2 (3:1).

Sediment samples were air dried and then were dried at 75^{o}C over 48 hours. The dried sediment samples were chopped in an agate mortar and sieved through a sieve <1.5 mm. The sediment samples were mineralized with a mixture of HCl: HNO_3 (3:1) in a microwave furnace, a Milestone Microwave Ethos 1 [9]. The water samples were filtered through a 0.45 μm Millipore filter and stored in 1L plastic bottles with the addition of 2 mL of HNO_3.

Determining the concentration of Co and Ni in the samples of water, sediments and plants was conducted by ICP-OES technique on a “Spectro Arcos” device.

The capacity of plants to absorb and accumulate metals from the growth media was evaluated using their bio-concentration factor (BCF). BCF was calculated as the ratio of the concentrations of metals in part of plant and water: $BCF = [Metal]_{part\ of\ plant}/[Metal]_{water}$ [10]. The ability of plants to transport metals from the roots to the shoot parts was assessed by the translocation ability (TA). Translocation ability is calculated as the ratio of the concentrations of metal in the part of the plant and its root: $TA=[Metal]_{part\ of\ the\ plant}/[Metal]_{root}$, and for *Ceratophyllum demersum* as the ratio of metal concentrations in the leaf and stem: $TA=[Metal]_{leaf}/[Metal]_{stem}$ [11].

3. RESULTS

The middle values of Co and Ni concentration in water and sediments of Skadar Lake with six test locations are given in Table 1.

These are recorded the low metal content in water. During the research period there were no seasonal variations means concentrations of metals in the water of Lake Skadar. There are significant spatial variations in the results as reflected in the high standard deviation.

During the research period (April-October), there are not recorded statistically significant temporal variation of the concentration of metals in the sediment, but they are spacious. The highest concentrations of Co and Ni were observed in samples of sediments left the mouth of the Moraca river, and the least were in sediments of Radus.

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Table 1. The seasonal minimum and maximum concentrations of metals in water (μg dm^{-3}) and sediment (mg kg^{-1}) and the mean concentration ± standard deviation

Metal		April	June	August	October
Water					
Co	min-max	0.24-0.81	0.21-0.69	0.38-0.84	0.32-0.91
	mean ± s.d.	0.52±0.22	0.49±0.19	0.57±0.26	0.56±0.31
Ni	min-max	0.28-0.89	0.37-0.96	0.38-0.98	0.43-1.08
	mean ± s.d.	0.71±0.38	0.68±0.30	0.71±0.27	0.74±0.38
Sediment					
Co	min-max	6.31-10.1	5.73-12.9	5.28-13.2	5.12-12.6
	mean ± s.d.	8.96±2.52	9.02±2.94	8.76±3.13	9.18±3.08
Ni	min-max	29.3-131	34.8-110	30.1-113	34.6-125
	mean ± s.d.	79.0±44.3	73.1±36.3	74.5±40.6	83.4±47.6

These are recorded the low metal content in water. During the research period there were no seasonal variations means concentrations of metals in the water of Lake Skadar. There are significant spatial variations in the results as reflected in the high standard deviation.

During the research period (April-October), there are not recorded statistically significant temporal variation of the concentration of metals in the sediment, but they are spacious. The highest concentrations of Co and Ni were observed in samples of sediments left the mouth of the Moraca river, and the least were in sediments of Radus.

3.1 Time and spatial variation of content of heavy metals in macrophytes of Lake Skadar

Results of metal content in individual parts tested macrophytes and seasons are given in Table 2.

Table 3 shows average values of Bioconcentration seasonal factors, BCF (whole plant/ water) of Co and Ni, by time and space and middle seasonal values of translocation factor, for the test macrophytes.

3.1.1. Cobalt (Co)

The concentration of Co in the analyzed macrophytes and their bioaccumulative ability are decreasing in the following order: *L. minor* > *C. demersum* > *P. australis*. In various macrophytes were observed different periods of the season of their greatest Co-accumulation. The highest concentrations of Co in *P. australis* were recorded in August, *C. demersum* in April a minor in October. During the season, the highest concentrations of Co were recorded in the roof of *P. australis* (5,57 mg kg^{-1}), in the leaf of *C. demersum* (5,82 mg kg^{-1}) and in the roof of *L. minor* (5,60 mg kg^{-1}). Looking middle seasonal values, the highest content of Co was at the root of *L. minor*, and the lowest in the stem of *P. australis*.

Translocation of cobalt in the *P. australis* is low. The average concentration ratio of Co stem/root during a test of the season is 0.05. Bonanno (2011) was found relatively low translocation of Co through the organs of *P. australis* (TF<0.07). Assia et al. (2004) in *P. australis* find similar relationship stem/root (TA = 0.03). However, cobalt is one of the most toxic metals, and the fact that generally the root absorbed Co, may mean that the root acts as a filter for an adverse effect on other organs plant [14].

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Table 2. Seasonal changes in metal concentrations (mg kg^{-1} of dry matter) in particular parts of macrophytes; minimum and maximum value and the mean concentration value ± standard deviation

Metal	Part od plant	Minimum and maximum value Mean value ± standard deviation April	June	August	October
Phragmites australis					
Co	root	0.40-0.90 0.60±0.19	0.20-2.96 1.34±1.03	3.86-8.20 5.57±1.98	2.58-5.40 3.71±1.03
	stem	0.04-0.09 0.06±0.02	0.05-0.13 0.09±0.04	0.07-0.29 0.16±0.09	0.04-0.24 0.14±0.08
	leaf	0.08-0.24 0.14±0.06	0.12-0.40 0.20±0.10	0.19-0.92 0.41±0.26	0.18-0.98 0.46±0.28
Ni	root	0.89-7.79 4.38±2.91	3.54-9.19 6.50±2.59	5.02-13.5 9.81±3.32	3.78-10.7 8.00±3.00
	stem	0.49-2.28 1.02±0.68	1.09-2.29 1.81±0.48	1.49-3.58 2.42±0.74	1.28-2.20 1.72±0.35
	leaf	0.30-2.16 1.31±0.65	0.50-2.39 1.52±0.72	1.09-2.96 2.11±0.61	1.96-4.46 3.00±1.08
Ceratophyllum demersum					
Co	stem	1.78-5.78 3.03±1.52	0.69-2.75 1.43±0.71	1.09-3.29 2.01±0.80	0.69-1.79 1.19±0.41
	leaf	2.06-7.63 5.82±2.06	1.48-3.86 3.14±1.01	1.68-5.18 3.65±1.28	1.48-5.24 2.92±1.56
Ni	stem	3.68-12.6 7.91±3.97	3.77-12.8 7.23±3.83	4.08-14.9 7.73±4.20	4.20-11.8 6.52±2.90
	leaf	9.04-26.2 16.1±7.52	6.48-22.0 13.6±5.48	8.73-26.1 17.1±6.69	9.35-28.5 15.4±7.24
Lemna minor					
Co	root			2.63-8.78 5.13±2.67	3.28-8.53 5.60±2.54
	leaf			1.89-4.84 3.62±1.26	2.57-7.39 5.11±2.28
Ni	root			7.69-18.9 11.3±5.18	7.33-17.6 11.6±4.64
	leaf			5.00-9.76 7.55±2.25	7.38-20.0 11.4±5.93

Table 3. Mean annual values of BCF for Co and Ni in the organs examined macrophytes (whole plant), with respect to water and mean annual values translocation factor, T

Metal	*Phragmites australis*	*Ceratophyllum demersum*	*Lemna minor*
BFC $_{whole\ plant/water}$			
Co	1981	5361	9009
Ni	5113	16092	14760
Translocation factor			
	$T_{leaf/root}$	$T_{leaf/stem}$	$T_{leaf/root}$
Co	0.11	2.03	0.81
Ni	0.28	2.11	0.82

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Al-Rahab (2006) followed the seasonal (monthly) changes of the concentration of Co in the tissues of *C. demersum*, which are somewise different from the results of our work. He was find an increase in concentration from January to June, then it decreases until August and September, then rises again until October and November, when it reaches a maximum, and finally decreases to December. Compared to other seasons, the highest bioconcentration has been recorded in the summer.

It is not completely clear which part of the Co content in the leaf of *L. minor* is present due to translocation from the roots and which from the absorption of water. However, due to higher concentrations of metals in the roof, it is likely to dominate the translocation process.

3.1.2. Nickel (Ni)

Content of Ni decreases in the following order: *C. demersum* > *L. minor* > *P. Australis*, watching the entire plant. Respectively, decreases the ability of plants Bioconcentration. The greatest amount of Ni (17,1 mg kg^{-1}) is present in the leaves of *C. demersum* in August, and the lowest in the stem of *P. australis* (1,02 mg kg^{-1}) in April. Seasonal distribution of Ni in plants is different. At *P. australis* Ni content increases and than falling to October. In *C. demersum* Ni content decreases from April to June, rising until August and than falling to October. Ni content in *L. minor* root changes significantly from August to October while in the leaf, for the same period, increases remarkably. The translocation of Ni in plants is also different. In *P. australis*, Ni mainly remains in the root, in *C. demersum* most part is translocated from the stem in the leaf, whereas in *L. minor* at the end of the season almost equal amounts of this metal are at the root and in the leaf. Mobility Ni in plants varies between species, from mobile in some plants [16,17] to the immobile in other [18]. In our testing of *P. australis*, the ratio of leaf/root and the stem/root is about 0.25, depending on the season, which is in correlation with the findings of other authors [19,20]. In contrast to the mentioned, Keller et al. (1998) and Baldantoni (2004) cite the ratio of leaf/root 0.03 and 0.02, respectively.

The content of Ni in the stem and the leaf of *C. demersum* slight decrease from April to June, rise until August and then again falling until October. Al-Rakabi (2006) also follows the seasonal (monthly) changes of the concentration of Ni in the tissues of *C. demersum* which shows a different trend compared to the results of our work.

Similar values of Ni content throughout the whole plant *L. minor*, which are similar to our own, find by Iram et al. (2012). This amount, according to these authors was 1–15 mgNi kg^{-1}. Khellaf and Zerdaoui (2009) report that the *L. minor* is tolerant to 3 mg dm^{-3} Ni in an aqueous medium, but the optimum growth is initiated on the 0.5 mg dm^{-3}. Zayed (1998) demonstrates that even a small amount of Ni accumulates in the tissues *L. minor* (1.79 g kg^{-1}), rom the medium containing 10 mgNi dm^{-3}. However, Axtell et al. (2003) talk about the benefits of duckweed in the accumulation of Ni.

4. CONCLUSIONS

Content of Co in the examined parts of macrophytes were in the range of 0.04-8.78 mg kg^{-1}. The concentration of Co decreases in the following order: *L. minor* > *C. demersum* > *P. australis*. Content of Ni in the examined parts of macrophytes were in the range of 0.30-28.5 mg kg^{-1}. The concentration of Ni decreases in the following order: *C. demersum* > *L. minor* > *P. australis*. In tissues *P. australis* and *L. minor*, cobalt and nickel are accumulated in the root for the most part, while in the tissues of *C.demersum* these two metals are largely found in stem. Cobalt and nickel are poorly mobile trough the bodies of *P.australis* and *L. minor*, while in *C. demersum* they showed considerable mobility from stem to leaf. The highest contents of the investigated metal in the organs of *P. australis* and *C. demersum* were recorded in the beginning and during the growing season. Higher concentrations of metals in the tissue of *L. minor* were observed at the end of the growing season.

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References

[1] Lodenius, M., 1991. Mercury concentrations in an aquatic ecosystem during twenty years following abatement the pollution source. *Water Air & Soil Pollution*, **56**, 323-332.

[2] Sasaki, K., Ogino, T., Hori O., Endo, Y., Kurosawa, K., Tsunekawa, M., 2003. Chemical Transportation of Heavy Metals in the Constructed Wetland Impacted by Acid Drainage. *Materials Transactions*, **44(2)**, 305-312.

[3] Jastrzębska, M., Cwynar P., Polechoński R., Skwara T., 2010. The Content of Heavy Metals (Cu, Ni, Cd, Pb, Zn) in Common Reed (*Phragmites australis*) and Floating Pondweed (*Potamogeton natans*). *Polish Journal of Environmental Studies*, **19(1)**, 243-246.

[4] Albers P.H., and Camardese, M.B., 1993. Effects of acidification on metal accumulation by aquatic plants and invertebrates. 1. Constructed wetlands. *Environtal Toxicology and Chemistry*, **12**, 959-967.

[5] Ayeni, O.O., Ndakidemi, P.A., Snyman R.G., Odendaal S., 2010. Chemical, biological and physiological indicators of metal pollution in wetlands (Review). *Scientific Research and Essays*, **5(15)**, 1938-1949.

[6] Brekken, A., Steinnes, E., 2006. Seasonal concentrations of cadmium and zinc in native pasture plants: consequences for grazing animals. *Science of the Total Environment*, **326**, 181–195.

[7] Bidar, G., Pruvot, Ch., Garçon, G., Verdin, A., Shirali P. and Douay, F., 2009. Seasonal and annual variations of metal uptake, bioaccumulation, and toxicity in Trifolium repens and Lolium perenne growing in a heavy metal-contaminated, field. *Environmental Science and Pollution Research*, **16(1)**, 42-53.

[8] Al-Yemni, M.N., Sher Hassan, El-Sheikh Mohamed A., and Eid Ebrahem, M., 2011. Bioaccumulation of nutrient and heavy metals by Calotropis procera and Citrullus colocynthis and their potential use as contamination indicators. *Scientific Research and Essays*, **6**, 966-976.

[9] USEPA Method 3051a., 2007. *Microwave assisted acid digestion of sediments, sludges, soils and oils*, Revision 1.

[10] Hawker, D., Connell, D., 1991. An evaluation between bioconcentration factor and aqueous solubility. *Chemosphere*, **23**, 231-241

[11] Deng, H., Ye, Z.H., Wong, M.H., 2004. Accumulation of lead, zinc, copper and cadmium by wetland plant species thriving in metal-contaminated sites in China. *Environmental Pollution*, **132**, 29-40

[12] Bonanno, G., 2011. Trace element accumulation and distribution in the organs of *Phragmites australis* (common reed) and biomonitoring applications. *Ecotoxicology and Environmental Safety*, **74**, 1057–1064.

[13] Assia A., El Falaky1 S.A., Aboulroos A.A., Saoud and Ali M.A., 2004. Aquatic plants for bioremediation of waste water. *In:Proceedings of Eighth International Water Technology Conference, IWTC8*, Alexandria, Egypt, p. 361-376.

[14] Shankers, A.K., Cervantes, C., Losa-Tavera, H., Avdainayagam, S., 2005. Chromium toxicity in plants. *Environmental International*, **31**, 739–753.

[15] Al-Rekabi, H.Y., 2006. Distribution of Cobalt and Nickle in plankton and its aquatic surround habitats in Euphrates and Al-Garaf rivers at Al-Nassiria city, southern of Iraq. *Journal of University of Thi-Qar*, **2(2)**, 8-15.

[16] Tiffin, L.O., 1971. Translocation of nickel xylem exudate of plants. *Plant Physiology*, **48**, 273-277.

[17] Thiesen, M.O., Blincoe, C., 1988. Isolation and partial characterization of nickel complexes in higher plants. *Biological Trace Element Research*, **16**, 239-251.

[18] Sajwan, K.S., Ornes, W.H., Youngblood, T.V., Alva, A.K., 1996. Uptake of soil applied cadmium, nickel and selenium by bush beans. *Water Air and Soil Pollution*, **91(3-4)**, 209-217.

[19] Borišev, M., Pajević, S., Stanković, Ž., Krstić, B., 2006. Macrophytes as phytoindicators and potential phytoremediators in aquatic ecosystems. Internat. Assoc. Danube Res. (IAD), 36th International Conference, Klosterneuburg & Vienna, The Book of Abstracts, p. 21.

[20] Al-Taisan, W. A., 2009. Suitability of Using *Phragmites australis* and *Tamarix aphylla* as Vegetation Filters in Industrial Areas. *American Journal of Environmental Sciences*, **5(6)**, 740-747.

[21] Keller, B., Lajtha K., Cristofor, S., 1998. Trace metal concentrations in the sediments and plants of the Danube delta, Romania. *Wetlands*, **18**, 42–50.

[22] Baldantoni, D., Alfani, A., Tommasi, P.D., Bartoli, G., De Santo, A.V., 2004. Assessment of macro and microelement accumulation capability of two aquatic plants. *Environmental Pollution*, **130**, 149-156.

[23] Iram, S., Ahmad I., Riaz, Y., and Zahara, A., 2012. Treatment of Wastewater by *Lemna minor*. *Pakistan Journal of Science*, **44**, 553-557.

[24] Khellaf, N., Zerdaoui, M., 2009. Growth Response of the Duckweed *Lemna minor* to Heavy Metal Pollition, Iranian Journal of Environmental Health Science & Engineering. 6(3), 161-166.

[25] Zayed, A., 1998. Phytoaccumulation of trace elements by wetland plants Duckweed. *Journal of Environmental Quality*, **27**, 715-721.

[26] Axtell, N.R., Sternberg, S.P.K., Claussen, K., 2003. Lead and nickel removal using *Microspora* and *Lemna minor*. *Bioresource Technology*, **89**, 41-48.

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Experimental studies on the toxicity and geno-cytotoxicity effects of cadmium in embryos and larvae of rainbow trout, *Oncorhynchus mykiss*

N. Kazlauskienė, Ž. Cibulskaitė*, M. Stankevičiūtė, J. Baršienė

Nature Research Centre, Akademijos str. 2, LT–08412 Vilnius, Lithuania
*Corresponding author: Email: ziwiliukx@gmail.com

Abstract

Cadmium (Cd) is one of the metals that have irrefutable negative effect to biota. The purpose of the study were: (1) to determine the 96-hour LC_{50} of Cd to rainbow trout *Oncorhynchus mykiss* embryos and larvae; (2) to investigate the toxic effect of Cd (2 μg Cd L^{-1} as $CdCl_2{\cdot}H_2O$) on biological parameters of rainbow trout in early ontogenesis (embryos and larvae) in relation with the duration of exposure; and (3) to evaluate geno-cytotoxicity potential in erythrocytes of the fish embryos and larvae exposure to Cd. Bioassay testing was conducted under controlled laboratory conditions. The 96-hour LC_{50} values of Cd were determined to embryos and larvae. Chronic test on fish at early stages of development (starting from "eye-egg" embryos 12-day before hatching and continued 12-day after hatching and including hatching period) was performed under static conditions. Several endpoints including mortality; function of the cardio-respiratory system; developmental disorders; hatching rate and cytogenetic damage [micronucleus (MN) and other nuclear abnormalities (NA) assays] in embryos and larvae were investigated. Cadmium at sublethal concentration showed a negative effect on the biological parameters of embryos and larvae which is related to the duration of exposure. Various developmental disorders were observed. Long-term exposure of embryos to Cd induced significant formation of MN and pooled cytotoxicity and caused significant increase of all geno-cytotoxicity endpoints analyzed in larvae erythrocytes. This is the first reported attempt to estimate different biological impacts on fish in early ontogenesis and herewith is an important step in understanding the Cd toxicity and geno-cytotoxicity mechanisms.

Keywords: cadmium; fish; embryos; larvae; toxicity; geno-cytotoxicity

1. INTRODUCTION

Heavy metal cadmium (Cd) is widely used in various modern industrial fields electroplating and galvanization processes in the production of pigments in batteries, as a chemical reagent, and in miscellaneous industrial processes and agriculture [1, 2]. Nanotechnology poses yet another risk for toxic Cd, which will now enter the biological realm in a nano-form [3]. The nanocrystal cores of many types of nanoparticles are miscible in water and contain the toxic metal Cd, so possible release of Cd from the nano-form cores presents an environmental concern [4].

Cd toxicity in different freshwater fish species has been extensively investigated by various scientists. Some authors demonstrated the morphological, physiological, hematological, biochemical and immunological changes in adult fish (*Clarias gariepinus*, *Oreochromis mossambicus*) experimentally treated with Cd [5, 2]. In addition, the Cd toxicity effects in developing fish may serve as important bioindicators for this type of pollution [6-9].

Cd has been reported to exert deleterious effects of nephrotoxicity, cytotoxicity, mutagenicity, genotoxicity, immunotoxicity, as well as, clastogenic, teratogenic, carcinogenic impacts in fish [10-

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13, 6]. Cd that enters aquatic environments accumulates within the tissues of aquatic organisms. The accumulation in the organisms depends on the concentration, route of absorption, environmental conditions and other intrinsic factors [14]. Cd has numerous adverse effects in fish reproductive processes, such as sexual maturation, spermatogenesis, fertilization success and development of the embryonic and post embryonic stages [15]. During the acute exposure of Cd, the freshwater fish showed some abnormal activities like erratic swimming, equilibrium loss and enhanced surfacing behavior [16]. Moreover, it has adverse effects on cellular defense systems and enzymes induce lipid peroxidation, DNA strand breaks, chromosome aberrations, disruption of DNA repair, and apoptosis [10, 11, and 13].

The molecular mechanisms underlying Cd toxicity and their specific effects on fish are poorly understood [7]. Cd in ionic form gain entry into cells by simple diffusion or through membrane carriers and ion channels [15]. According to Bougas and co-authors [7] this metal can affect the transcription level of genes involved in iron metabolism, vitamin metabolism, blood coagulation, and calcium transport.

In recent years, early fish development studies have gained interest amongst researchers because of their high sensitivity to pollutants and their ecological relevance [15]. Our research focuses on nanoparticle (quantum dots) and heavy metal toxicity mechanisms in developing fish, in particular, the Cd toxicity and geno-cytotoxicity effects in early fish development. The comprehensive investigation of biological impacts in early fish development is an important step in understanding the Cd toxicity and geno-cytotoxicity mechanisms.

The main aims of the study were: (1) to determine the 96-hour LC_{50} of Cd to rainbow trout *Oncorhynchus mykiss* embryos and larvae; (2) to investigate the toxic effect of Cd (2 μg Cd/L as $CdCl_2{\cdot}H_2O$) on biological parameters in early development in relation to the duration of exposure; and (3) to evaluate geno-cytotoxicity potential of Cd in erythroblasts of the fish embryos and larvae.

2. MATERIALS AND METHODS

2.1 Test-object

The toxicity study was performed at the Laboratory of Ecology and Physiology of Hydrobionts (Nature Research Centre). Rainbow trout (*Oncorhynchus mykiss*) embryos were obtained as eyed eggs from the Simnas experimental hatchery (Alytus District, Lithuania).

2.2 Bioassay testing

Bioassay testing was carried out under controlled laboratory conditions. The tests on fish embryos and larvae were performed accordance with guidelines presented in ISO standards (ISO 7346-1:1996, ISO 12890:1999). Studies have been carried out with non-protected life-stages accordance with EU Directive 2010/63/EU. Acute test (96-hour) on fish at early stages of development [starting from "eye-egg" embryos (96-hour before hatching) – the first test; hatched larvae at hatching period – the second test (the first test continue); and starting from 1-day old larvae – the third test] were performed under semi static conditions. Control water and test solutions in aquaria were additionally aerated/changed at 24-hour intervals. Chronic tests: 12-day (starting from "eye-egg" embryos 12-day before hatching) on embryos and 24-day (starting from "eye-egg" embryos 12-day before hatching and continued 12-day after hatching and including hatching period) on larvae were performed under static conditions. All tests were performed in the climatic camera (Bronson PGC-660, Germany). Studies with embryos and larvae were performed in two replications (N = 20 in each group).

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2.3 Water chemical and physical characteristics

Deep-well water was used for dilution and control test [17]. Dissolved oxygen in the glass aquaria, temperature, pH and conductivity were measured routinely with a hand-held multi-meter (WTW Multi 340i/SET, Germany).

2.4 Tests-parameters

Biological parameters as mortality, physiological (cardio-respiratory), such as heart rate (HR, counts/min), gill ventilation frequency (GVF, counts/min), hatching rate (%), blood circulatory system development disorders (%) of embryos and larvae were investigated. Blood circulation system was viewed using stereomicroscope (Meiji Techno RZ Series, Japan), and observed abnormalities and lesions were registered by Nikon Cool pix 995 digital camera (Japan). The number of hatched eggs and the mortality of embryos and larvae were monitored and recorded daily. Other parameters of embryos and larvae were monitored and recorded after 1, 4, 8 and 12 days. Mortalities and hatching rates were then recorded during hatching period (1-6-day). Total number of eggs in each treatment was 20 fertilized eggs (two replications). Unfertilized eggs were approximately 2%.

2.5 The concentration of Cd

Reagent grade cadmium chloride ($CdCl_2 \cdot H_2O$) («REACHIM» Company, Russia) was used as the toxicant and stock solutions were prepared by dissolving a necessary amount of salts in distilled water. The concentrations in acute test were 0.5; 1.0; 2.0; 4.0; 8.0 μg Cd/L. The concentration of 2 μg Cd/L was chosen according to the 96-hour LC50 for rainbow trout larvae (Table 1). Nominal Cd concentrations were checked with an atomic absorption spectrophotometer (SHIMADZU AA-6800, Japan). Mean measured concentrations were within 5% of target [17].

2.6 Micronucleus (MN) and nuclear abnormalities (NA) assays

Induction of micronuclei (MN), nuclear buds (NB), bi-nucleated (BN), fragmented-apoptotic (FA) cells were analysed in erythroblasts of embryos and larvae. Cell smears were prepared from whole embryos and larvae (with removed yolk sac) body (gently nipped with tweezers): directly smeared on glass slides and air-dried. Smears were fixed in methanol for 10 min. and later were stained with 10 % Giemsa solution in phosphate buffer pH = 6.8 for 20 - 40 min. The stained slides were analysed under light microscopes Olympus BX51 at final magnification of 1,000×. Micronuclei and other NA were identified following criteria described by Fenech et al. [18]. The frequencies of abnormalities were recorded in 1,000 erythroblasts per slide using blind scoring by a single observer.

2.7 Statistical analyses

The 96-hour Median-Lethal-Concentration (LC50) values and their 95 % confidence intervals were estimated using the trimmed Spearman-Karber method [19]. Means and standard deviations were calculated for embryos and larvae to each studied parameter. Differences between the evaluated characteristics studied were tested by two-way ANOVA at $p < 0.05$ using Statistica 7.0 software's (USA). Pearson correlation analysis was performed to identify possible relationships between biological parameters of embryos and larvae and the duration of exposure. Micronucleus and nuclear abnormalities assays were evaluated by non-parametric Mann-Whitney *U*-test (GraphPad Prism 5, USA). Differences were accepted as significant at the 95% level of confidence ($p < 0.05$).

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3. RESULTS AND DISCUSSION

3.1 Acute toxicity

Mortality of embryos/larvae increased with increasing Cd concentration. The highest mortality of embryos was observed at 8 μg Cd/L, where 97.5 % embryos died during exposure period (first test). In the exposure period 96-hour at 4 μg Cd/L 90 % of hatched larvae (second test) and 89 % of larvae (third test) were dead (Table 1). The calculated 96-hour LC50 values of Cd for rainbow trout embryos/larvae were: 3.32, 1.14, and 2.23 μg Cd/L, respectively. The larvae were consistently more sensitive than the embryos. The most sensitive were hatched larvae.

Eaton with co-authors [20] found that concentrations ranging from 4 to 12 μg Cd/L were fatal to the embryos and larvae of freshwater fish. Fish at early stages of development are more sensitive to toxicants [21]. The larvae were consistently more sensitive than the embryos [20]. Jezierska and co-authors [14] indicated that hatching is a particularly sensitive developmental period. The difference in sensitivities is most likely due to a chorion protecting the embryonic fish [21]. During embryonic development, the embryos are protected by the egg shell and so the chance of metals entering into the egg is relatively small [14].

Table 1 Acute toxicity of Cd to rainbow trout in early life stages

Test	Rainbow trout (*Oncorhynchus mykiss*)	96-hour LC50 (μg Cd/L)	0.95 confidence interval (μg Cd/L)
First (start from eyed embryos 96-hour before hatching)	Eye-stage embryos	3.32	2.67-4.13
Second (continuous first test included hatching period)	Hatched larvae	1.14	0.72-1.56
Third (start from 1-day old larvae)	Hatched larvae	2.23	1.78-2.79

3.2 Chronic toxicity

3.2.1 Mortality

The concentration of 2 μg Cd/L induced a significant ($p < 0.05$) increase in mortality of embryos (chronic test 12-day) after 1-, 4-, 8- and 12-day of exposure, ranging from 6.4 ± 1.1 % to 15.5 ± 1.7 % (in control mortality was from 0.0 ± 0.0 % to 5.2 ± 0.6 %). Mortality of embryos significantly increased ($p < 0.05$) with the exposure duration (12-day) compared to the 1-day exposure (Table 2 and Figure 1a).

Treatment with 2 μg Cd/L had profound effects on the overall health conditions of the larvae (chronic test 24-day). After 1-, 4-, 8- and 12-day exposure the mortality of larvae significant increased ($p < 0.05$) to 25.8 ± 1.2; 36.7 ± 4.7; 49.2 ± 13.0; 49.2 ± 13.0 %, respectively, compared to the control (control respective values 0.0 ± 0.0 to 2.5 ± 3.5 %; Table 4 and Figure 1a). Mortality of larvae significantly increased ($p < 0.05$) with the increase in the exposure duration (4-, 8- and 12-day) compared to the 1-day exposure (Table 3 and Figure 1a).

Mortality of embryos and larvae of various fish species due to Cd exposure has been reported before. Mortality was observed in embryos and pro-larvae of *Silurus soldatovi* exposed to various concentrations of Cd [22]. According to Ismail and Yusof [23], exposure of fertilized eggs of *Oryzias javanicus* to 100 μg Cd/L completely inhibited development and resulted in death of all embryos. Cd was also observed to cause higher mortality of newly hatched larvae than embryos [14]

Table 2 Chronic effect of Cd on rainbow trout embryos mortality and HR

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in relation with the duration of exposure (mean ± SD)

Exposure days	Parameters	
	Mortality % (N = 38)	**HR counts/min (N = 20)**
Cd (2 µg Cd/L)		
1	6.4 ± 1.1*#	77.6 ± 6.5*#
4	6.4 ± 1.1*#	78.8 ± 5.3*#
8	9.1 ± 2.8*#	85.2 ± 6.5*
12	15.5 ± 1.7*	88.0 ± 5.7*
Control		
1	0.0 ± 0.0	95.2 ± 6.5
4	0.0 ± 0.0	94.4 ± 6.3
8	5.2 ± 0.6	95.2 ± 2.5
12	5.2 ± 0.6	96.0± 3.3

* Significantly different from control ($p < 0.05$); # Significantly different between the duration of exposure compared with the 12-day exposure ($p < 0.05$)

Table 3 Chronic effect of Cd on rainbow trout larvae in relation with the duration of exposure (mean ± SD)

Exposure days	Parameters		
	Mortality % (N = 37)	**GVF counts/min (N = 20)**	**HR counts/min (N = 20)**
Cd (2 µg Cd/L)			
1	25.8 ± 1.2*	88.0 ± 6.5*	97.6 ± 5.7*
4	36.7 ± 4.7*#	97.2 ± 7.6*#	93.2 ± 8.4*
8	49.2 ± 13.0*#	118.4 ± 4.2*#	97.6 ± 9.6
12	49.2 ± 13.0*#	127.6 ± 6.2*#	116.8 ± 7.3*#
Control			
1	0.0 ± 0.0	104.8 ± 6.5	109.6 ± 5.4
4	0.0 ± 0.0	108.0 ± 6.5	106.0 ± 3.9
8	2.5 ± 3.5	110.0 ± 6.4	104.0 ± 4.1
12	2.5 ± 3.5	113.6 ± 7.4#	109.6 ± 6.3

* Significantly different from control ($p < 0.05$); # Significantly different between the duration of exposure compared with the 1-, 2-, 4-day exposure ($p < 0.05$)

3.2.2 Cardio-respiratory parameters

The concentration of 2 µg Cd/L significantly decreased heart rate (HR) of embryos during the entire test (chronic test 12-day) (Table 2, Figure 1b). HR of embryos during 12-day exposure was within the range 77.6 ± 6.5–88.0 ± 5.7 counts/min (in control 96.0 ± 3.3 counts/min). HR of embryos exposed to only 1- and 4-day Cd was significantly ($p < 0.05$) different from 12-day exposure.

Cd induced a significant ($p < 0.05$) decrease in HR of larvae during 1- and 4-day (chronic test 24-day) and were within the range 93.2 ± 8.4–97.6 ± 5.7 counts/min (Table 3, Figure 1c). Meanwhile, after 12-day exposure HR of larvae significantly increased ($p < 0.05$) to 116.8 ± 7.3 counts/min as compared to control (109.6 ± 6.3 counts/min) (Table 3, Figure 1b). It was found that

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HR of larvae significantly ($p < 0.05$) increased only on the 12-day of exposure (compared with stable HR during the 1-, 4- and 8-day exposure).

Significantly ($p < 0.05$) decreased gill ventilation frequency (GVF) of larvae after 1- and 4-day of exposure of 88.0 ± 6.5, 97.2 ± 7.6 counts/min, respectively (in control 104.8 ± 6.5; 108.0 ± 6.5 counts/min) (Table 3 and Figure 1d) was observed (chronic test 24-day). After 12-day exposure GVF of larvae significantly increased ($p < 0.05$) to 127.6 ± 6.2 counts/min comparing to control - 113.6 ± 7.4 counts/min. It was found that respiratory parameters of larvae were significantly ($p < 0.05$) related to the duration of exposure. GVF of larvae was significantly induced ($p < 0.05$) with the increase in the duration of exposure (Table 3, Figure 1c).

The Pearson correlation analysis of mortality, HR, GVF and the duration of exposure (1-, 4-, 8- and 12-day) of embryos and larvae showed a positive correlation. Strong correlation between mortality and the duration of exposure of embryos (r = 0.88) and larvae (r = 0.77); between HR and the duration of exposure of embryos (r = 0.60) as well as larvae (r = 0.61); and between GVF and the duration of exposure of larvae (r = 0.92) were found.

According to Reddy and Reddy [24] cadmium chloride caused negative effects on opercular beats/minute of *Catla catla*. The differences between means of opercular beats of exposed and control fish were highly significant at 24, 48, 72 and 96 hours exposure periods. It was pointed that Cd induced gill necrosis in fish, which may also be a cause of decrease in oxygen consumption and increase in ventilation frequency [24]. Jezierska et al. [14] study revealed that Cd exposure caused an increase in HR of embryos and larvae of common carp and grass carp. HR is a reliable indicator of metabolic rate in embryos [14].

3.2.3 Developmental disorders

In our study, 8-day exposure of rainbow trout eyed embryos (test started 12-day before hatching) to 2 µg Cd/L resulted in visible embryonic haemorrhage in the head area ~14 ± 1.4 % that was significantly different ($p < 0.05$) from control (Figure 2a). Meanwhile, even after 4-day exposure of larvae to the same concentration of Cd various developmental disorders were found (Figure 1a, b, c and d). During 4- and 12-day blood clot was the most visible in larval head area and in other parts of the body: around the eyes, in the yolk sac or in the dorsal fin (29 ± 1.4 % larvae, significantly different ($p < 0.05$) from control (Figure 2b). Spine curvature deviations ~5 ± 1.4 % (Figure 2c) and yolk sac edema ~6.5 ± 2.1 % (Figure 2d) were observed in larvae of rainbow trout (in control 2.5 ± 3.5 %).

Malformations of the yolk sac and curvature in the abdominal region were also observed throughout El-Greisy and El-Gamal [25] study. The impact of heavy metals was the most pronounced during the hatching process of common carp. Embryonic deformations in common carp like spine curvature, incomplete eye pigmentation, lack of tail, lack of head were the most commonly observed. The newly hatched larvae showed severe body malformation, and they were not able to swim or feed [25]. Sublethal effects in fish, notably malformation of the spine, have been reported [6]. More specifically, Cd affected genes involved in the blood coagulation cascade, calcium ion binding and apoptosis [7].

3.2.4 Hatching rate

The percentage of egg hatching rate was recorded during the hatching period (1-6-day) (Table 4, Figure 1d). The hatching rate in the larvae was significantly ($p < 0.05$) lower for the treated group when compared with control. Meanwhile, the duration of exposure and larvae hatching period had significantly ($p < 0.001$) correlated (r = 0.95).

The El-Greisy and El-Gamal [25] study indicated that the fertilization and hatching rates as well as the development of the embryos of common carp were adversely affected by heavy metal treatment. The percentage of fertilization and hatching rates and deformed eggs were recorded 96-hour post-hatching. When compared to the control group, it was found that the both rates in the larvae treated with 0.03 and 0.06 mg of $CdCl_2$/L had decreased. Fertilization and hatching rates decreased in

relation to the increase in the concentration of the heavy metals [25]. Other investigators observed the acceleration of larvae hatching after exposure to a high concentration of Cd (0.2 mg Cd/L or higher) [14, 26]. Thus it is possible that Cd damaged the hatching glands, disturbed the egg envelope hardening, and could act as an additive activator of chorionase (due to the chemical similarity of Cd and calcium) or oxygen deficit in water could cause the acceleration of hatching [26].

Table 4 Effect of Cd on the hatching rate (1-6-day during hatching) in rainbow trout eggs

Experimental	Hatching rate (%)					
trials	1-day	2-day	3-day	4-day	5-day	6-day
Cd	0.0±0.0	3.6±5.1	22.6±8.4*	53.6±5.1*	59.9±6.2*	62.7±2.2*
Control	2.4±3.4	5.2±0.6	63.9±3.9	89.7±1.8	94.8±0.6	94.8±0.6

* Significantly different from control (p < 0.05)

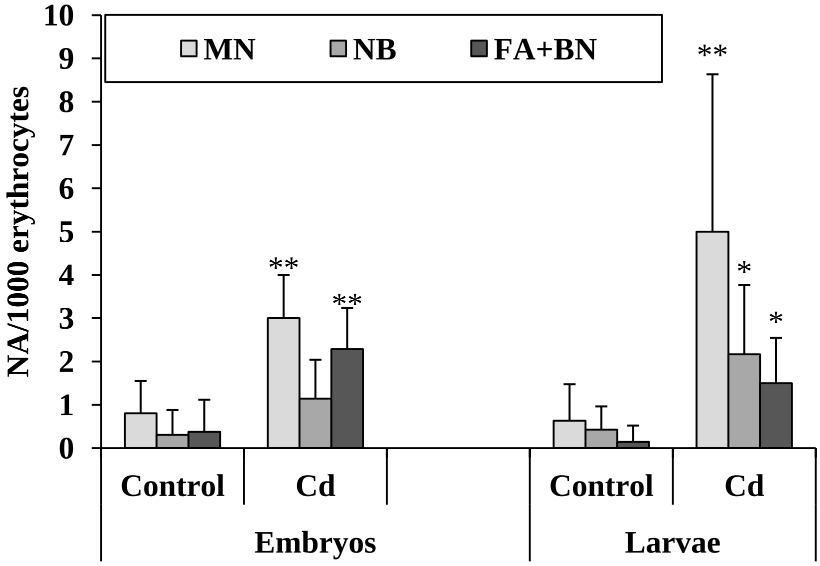


Figure 1. The frequency of micronuclei (MN), nuclear buds (NB) and fragmented-apoptotic (FA) + bi-nucleated (BN) cells in erythroblasts of 4-day embryos and larvae. Differences between control and exposed groups shown: *p < 0.05; **p < 0.005.

3.2.5 Micronucleus (MN) and nuclear abnormalities (NA) assays

Cd exposure caused both genotoxic and cytotoxic effects during developmental periods of rainbow trout (Figure 1). After 96-hour exposure to Cd, significant elevation of MN and pooled cytotoxicity (bi-nucleated (BN) + fragmented-apoptotic (FA) cells) were detected in the embryo erythroblasts. Micronuclei and NB frequencies increased approximately 4 times, pooled cytotoxicity increased 6 times compared to the control levels. The long-term exposure of larvae to Cd significantly induced the formation of MN, NB and pooled cytotoxicity (Figure 2 g-j). Micronuclei, NB and pooled cytotoxicity frequencies increased approximately 8, 5, 11 times, respectively compared to control level. This study confirms that the MN and NA assays can be used successfully to detect Cd genotoxicity and cytotoxicity in erythroblasts from whole embryos and larvae.

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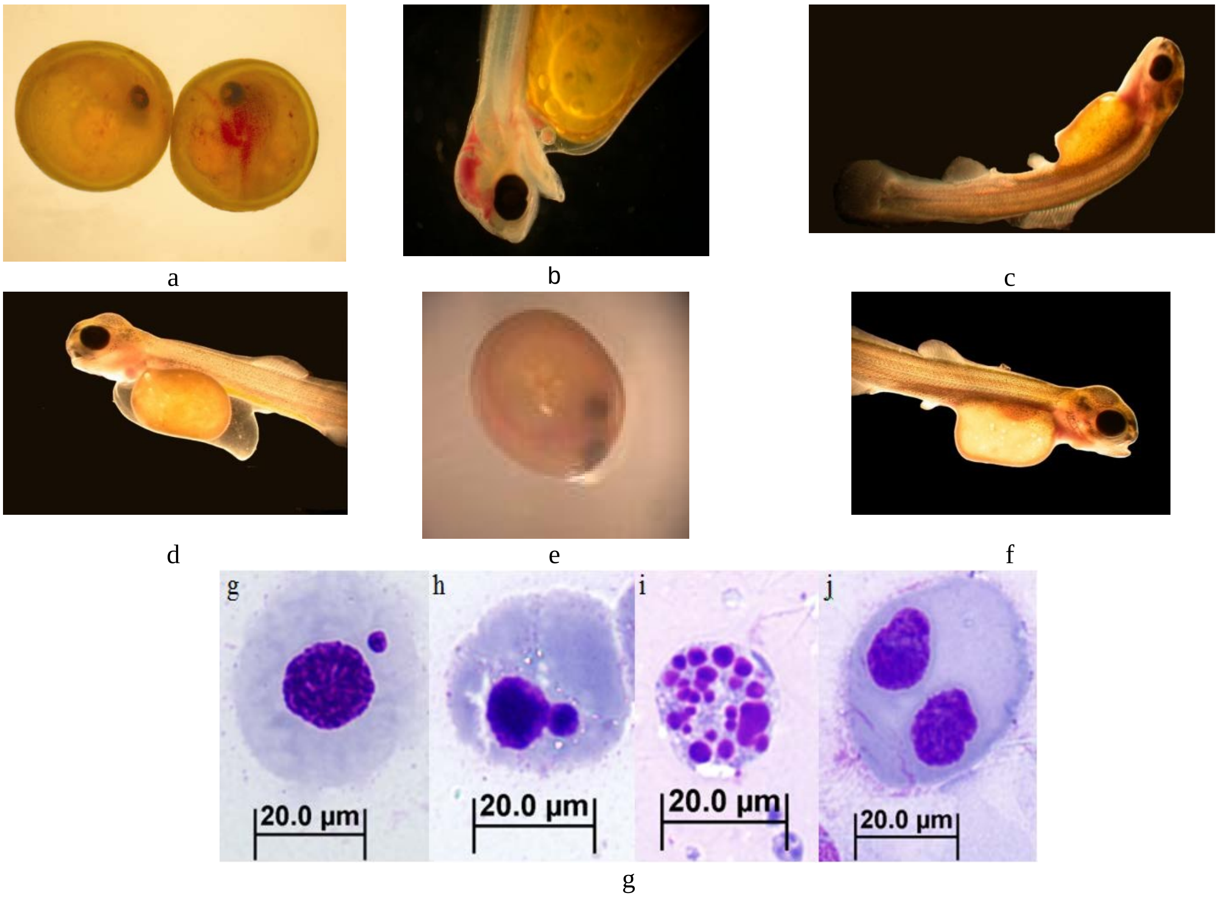


Figure 2. Development disorders induced by Cd: (a) haemorrhage in embryos, (b) blood clot in head, (c) spine curvature, (d) yolk sac edema of embryos and larvae of rainbow trout during exposure of Cd (chronic tests 12-, 24-day), (e) normal embryos, (f) normal larvae; larvae erythroblasts with (g) micronucleus (MN), (h) nuclear bud (NB), (i) fragmented-apoptotic (FA) erythroblast, (j) bi-nucleated (BN) erythroblast.

3.2.5 Micronucleus (MN) and nuclear abnormalities (NA) assays

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The micronucleus assay is the most widely used assay for the detection of chromosomal aberrations and other genotoxicological endpoints *in vivo*. Increased frequencies of micronucleated and binucleated cells in fish tissues exposed to Cd were recorded by many authors [11, 27]. Güner and Muranlı [28] reported significant elevation of total nuclear abnormalities (notched, lobed, bud, fragmenting) in erythrocytes of *Gambusia affinis* following exposure to 0.1 ppm and 1 ppm of Cd for one and two weeks. Chronic exposure to $CdCl_2$ (0.37 and 0.62 mg/L) induced elevated formation of micronuclei and other nuclear abnormalities (nuclear bud, binucleates, lobed, notched and vacuolated nuclei) in peripheral blood erythrocytes of fish *Labeo rohita* [27]. Cd induced cell death by apoptosis was determined in rainbow trout hepatocytes [29].

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Several investigations have demonstrated that embryo or larvae life stage responds to known DNA damaging agents. DNA damage caused by Cd in early fish development was emphasized in several fish species. The genotoxicity potential of Cd in the sediments (from 1.9 μg/g) on Japanese medaka (*Oryzias latipes*) embryos, of $CdCl_2$ (0.112 - 11.2 mg/L) on embryonic zebrafish cells ZF4 and of $CdCl_2$ (0.1 μM) on *O. latipes* larvae was investigated by Barjhoux et al. [30], Pereira et al. [31], Morin et al. [32], respectively. Risso-de Faverney with co-authors [32] determined that Cd induced apoptosis and DNA strand breaks in trout hepatocytes that are partially provoked by the generation of ROS. According to Hsu et al. [33] study, Cd at sublethal levels induced oxidative stress in zebrafish (*Danio rerio*) embryos. Consequently, oxidative stress and DNA repair inhibition are major mechanisms triggering Cd genotoxicity [33].

Summarizing the study results, we demonstrated that laboratory – controlled assessment of toxicity and geno-cytotoxicity effects can provide new information and accurate assessment about Cd exposure impact on fish in early stages of development. Based on the obtained results, we demonstrate that Cd induced geno-cytotoxicity, reduced survival, and disturbed cardio-respiratory system activity, affected development and hatchability of fish in early life stages causing negative consequences for the well-being of the fish populations and communities. Further investigation of the sublethal concentration Cd toxicity to fish in early stages of development could be a useful approach in assessment of ecological risk of heavy metals in aquatic ecosystems.

4. CONCLUSIONS

The calculated 96-hour LC50 values of Cd for rainbow trout embryos/larvae were: 3.32, 1.14, and 2.23 µg Cd/L, respectively (acute toxicity test). The larvae were consistently more sensitive than the embryos. The most sensitive were hatched larvae. Chronic tests (12-, 24-day) on rainbow trout at early stages of development results showed that Cd at sublethal concentration had a negative effect on the biological parameters of embryos and larvae and disturbs the vital functions of organism: significant ($p<0.005$) increased mortality, disturbed the cardio-respiratory system activity, hatching rate and observed various developmental disorders (haemorrhage in embryos; blood clots, yolk sac edema, and spine curvature in larvae). Mortality of larvae significantly increased ($p < 0.05$) with the increase in the duration of exposure. It was found that respiratory parameters of larvae significant ($p < 0.05$) depended on the duration of exposure. GVF of larvae 1-, 4-day significant decreased and 8-, 12-day increased ($p < 0.05$) with the increase on the duration of exposure. The Pearson correlation analysis of mortality, HR, GVF and the duration of exposure (1-, 4-, 8- and 12-day) of embryos and larvae showed a positive correlation. Strong correlation between mortality and the duration of exposure of embryos ($r = 0.88$) and larvae ($r = 0.77$); between HR and the duration of exposure of embryos ($r = 0.60$) as well as larvae ($r = 0.61$); and between GVF and the duration of exposure of larvae ($r = 0.92$). The 96-hour exposure of embryos to Cd induced significantly increased ($p < 0.005$) formation of MN and pooled cytotoxicity [bi-nucleated (BN) + fragmented-apoptotic (FA) cells]. The long-term Cd exposure caused significant ($p < 0.005$) increase of all analysed geno-cytotoxicity endpoints (MN, NB and pooled cytotoxicity) in larvae erythroblasts.

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References

[1] Raj, V.M., Thirunavukkarasu, A.R., Kailasam, M., Muralidhar, M., Subburaj, R., Stalin, P., 2013. Acute Toxicity Bioassays of Cadmium and Mercury on the Juveniles of Asian seabass *Lates calcarifer* (Bloch). *Indian Journal of Science and Technology*, **6 (4)**, 4330–4335.

[2] El-Said El-Boshy, M., Gadalla, H.A., El-Hamied, F.M.A., 2014. Immunological, hematological and biochemical changes induced by short term exposure to cadmium in catfish (*Clarias gariepinus*). *Journal of Coastal Life Medicine*, **2 (3)**, 175–180.

[3] Rzigalinski, B.A., Strobl, J.S., 2009. Cadmium-containing nanoparticles: Perspectives on pharmacology and toxicology of quantum dots. Toxicology and Applied Pharmacology, **238 (3)**, 280–288.

[4] Leigh, K.L., Bouldin, J.L., Buchanan, R.A., 2014. Measurement of Accumulation of Semiconductor Nanocrystal Quantum Dots by Pimephales Promelas. *Dose-Response: An International Journal*, **10 (3)**, 331–334.

[5] Benjamin, D., Thatheyus, A.J., 2012. Acute Toxicity of Nickel and Cadmium to the Cichlid Fish, *Oreochromis mossambicus* (Peters). *Research in Zoology*, **2 (4)**, 19–22.

[6] Okocha, R.C., Adedeji, O.B., 2011. Overview of Cadmium Toxicity in Fish. *Journal of Applied Sciences Research*, **7 (7)**, 1195–1207.

[7] Bougas, B., Normandeau, E., Pierron, F., Campbell, P.G.C., Bernatchez, L., Couture, P., 2013. How does exposure to nickel and cadmium affect the transcriptome of yellow perch (*Perca flavescens*) – Results from a 1000 candidate-gene microarray. *Aquatic Toxicology*, **142–143**, 355–364.

[8] Heydarnejad, M.S., Khosravian-Hemamai, M., Nematollahi, A., 2013. Effects of cadmium at sub-lethal concentration on growth and biochemical parameters in rainbow trout (*Oncorhynchus mykiss*). *Irish Veterinary Journal*, **66**, 11.

[9] Rani, S., Gupta, R.K., Rani, M., 2015. Heavy Metal Induced Toxicity in Fish with Special Reference to Zinc and Cadmium. *International Journal of Fisheries and Aquatic Studies*, **3 (2)**, 118–123.

[10] *Waalkes, M.P.*, 2000. *Cadmium carcinogenesis in review. Journal of Inorganic Biochemistry*, **79,** 241–*244.*

[11] Cavas, T., Garanko, N.N., Arkhipchuk, V.V., 2005. Induction of micronuclei and binuclei in blood, gill and liver cells of fishes subchronically exposed to cadmium chloride and copper sulphate. *Food and Chemical Toxicology*, **43**, 569–574.

[12] Kensova, R., Blazkova, I., Vaculovicova, M., Milosavljevic, V., Blazkova, L., Hynek, D., Kopel, P., Novotna, M., Zehnalek, J., Pohanka, M., Trnkova, L., Adam, V., Kizek, R., 2015. The Effect of Cadmium Ions and Cadmium Nanoparticles on Chicken Embryos and Evaluation of Organ Accumulation. *International Journal of Electrochemical Science*, **10**, 3623–3634.

[13] Mahrous, K.F., Hassan, A.M., Radwan, H.A., Mahmoud, M.A., 2015. Inhibition of cadmium - induced genotoxicity and histopathological changes in Nile tilapia fish by Egyptian and Tunisian montmorillonite clay. *Ecotoxicology and Environmental Safety*, **119**, 140–147.

[14] Jezierska, B., Ługowska, K., Witeska, M., 2009. The effects of heavy metals on embryonic development of fish (a review). *Fish physiology and biochemistry*, **35**, 625–640.

[15] Annabi, A., Said, K., Messaoudi, I., 2013. Cadmium: Toxic Effects and Physiological Impairments in Fishes. *International Journal of Advanced Research*, **1 (3)**, 372–382.

[16] Batool, M., Abdullah, S., Javed, M., 2014. Behavioral Intoxication of *Channa marulius* and *Wallago attu* during Acute Exposure of Cadmium and Copper. *Pakistan Journal of Life and Social Sciences*, **12 (1)**, 7–15.

[17] Svecevičius, G., 2010. Acute toxicity of nickel to five species of freshwater fish. *Polish Journal of Environmental Studies*, **19 (2)**, 453–456.

[18] Fenech, M., Chang, W.P., Kirsch-Volders, M., Holland, N., Bonassi, S., Zeiger, E., 2003. HUMN project: detailed description of the scoring criteria for the cytokinesis-block micronucleus assay using isolated human lymphocyte cultures. *Mutation Research*, **534**, 65–75.

[19] Hamilton, M. A, Russo, R. C, Thurston, R. V., 1977. Trimmed Spearman-Karben method for estimating median lethal concentration in toxicity bioassays. *Environmental Science & Technology*, **11 (7)**, 714–719.

[20] Eaton, J.G, McKim, J.M, Holcombe, G.W., 1978. Metal toxicity to embryos and larvae of seven freshwater species – I. Cadmium. *Bulletin of Environmental Contamination and Toxicology*, **19**, 95–103.

[21] Kazlauskienė, N., Vosylienė, M.Z., 2008. Characteristic features of the effect of Cu and Zn mixture on rainbow trout *Oncorhynchus mykiss* in ontogenesis. *Polish Journal of Environmental Studies*, **17 (2)**, 291–293.

[22] Zhang, H., Cao, H., Meng, Y., Jin, G., Zhu, M., 2012. The toxicity of cadmium (Cd_2) towards embryos and pro-larva of Soldatov's catfish (*Silurus soldatovi*). *Ecotoxicology and Environmental Safety*, **80**, 258–265.

[23] Ismail, A., Yusof, S., 2011. Effect of mercury and cadmium on early life stages of Java medaka (*Oryzias javanicus*): a potential tropical test. *Marine Pollution Bulletin*, **63**, 347–349.

[24] Reddy, J.S., Reddy, D.C., 2013. Impact of Cadmium toxicity on Behavioural and Haematological Biomarkers of Freshwater Fish, *Catla catla*. *International Journal of Bioassays*, **02 (09)**, 1199–1204.

ISBN: 978-960-6865-94-7

[25] El-Greisy, Z.A., El-Gamal, A.H.A., 2015. Experimental studies on the effect of cadmium chloride, zinc acetate, their mixture and the mitigation with vitamin C supplementation on hatchability, size and quality of newly hatched larvae of common carp, *Cyprinus carpio. The Egyptian Journal of Aquatic Research*, **41 (2**), 219–226.

[26] Szczerbik, P., Mikołajczyk, T., Sokołowska-Mikołajczyk, M., Socha, M., Chyb, J., Epler, P., 2008. The influence of cadmium on Prussian carp oocyte maturation, development of eggs and hatching. *Czech Journal of Animal Science*, **53 (1)**, 36–44.

[27] Jindal, R., Verma, S., 2015. *In vivo* genotoxicity and cytotoxicity assessment of cadmium chloride in peripheral erythrocytes of *Labeo rohita* (Hamilton). *Ecotoxicology and Environmental Safety*, **118**, 1–10.

[28] Güner, U., Muranlı, F.D.G., 2011. Micronucleus test, nuclear abnormalities and accumulation of Cu and Cd on *Gambusia affinis* (Baird & Girard, 1853). *Turkish Journal of Fisheries and Aquatic Sciences*, **11**, 615–622.

[29] Risso-de Faverney, C., Devaux, A., Lafaurie, M., Girard, J.P., Bailly, B., Rahmani, R., 2001. Cadmium induces apoptosis and genotoxicity in rainbow trout hepatocytes through generation of reactive oxygene species. *Aquatic Toxicology*, **53 (1)**, 65–76.

[30] Barjhoux, I¨, Baudrimont, M., Morin, B., Landi, L., Gonzalez, P., Cachot, J., 2012. Effects of copper and cadmium spiked-sediments on embryonic development of Japanese medaka (*Oryzias latipes*). *Ecotoxicology and Environmental Safety*, **79**, 272–282.

[31] Pereira, S., Cavalie, I., Camilleri, V., Gilbin, R., Adam-Guillermin, C., 2013. Comparative genotoxicity of aluminium and cadmium in embryonic zebrafish cells. *Mutation Research*, **750 (1–2)**, 19–26.

[32] Morin, B., Filatreau, J., Vicquelin, L., Barjhoux, I., Guinel, S., Leray-Forget, J., Cachot, J., 2011. Detection of DNA damage in yolk-sac larvae of the Japanese Medaka, Oryzias latipes, by the comet assay. *Analytical and Bioanalytical Chemistry*, **399 (6)**, 2235–2242.

[33] Hsu, T., Huang, K.M., Tsai, H.T., Sung, S.T., Ho, T.N., 2013. Cadmium (Cd)-induced oxidative stress down-regulates the gene expression of DNA mismatch recognition proteins MutS homolog 2 (MSH2) and MSH6 in zebrafish (*Danio rerio*) embryos. *Aquatic Toxicology*, **126**, 9–16.

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Long-term toxicity and geno-cytotoxicity of quantum dots to rainbow trout *Oncorhynchus mykiss* embryos

Ž. Cibulskaitė[1], M. Stankevičiūtė[1*], N. Kazlauskienė[1], J. Baršienė[1], V. Kulvietis[2], R. Rotomskis[2,3]

[1]Institute of Ecology of Nature Research Centre, Akademijos st. 2, LT-08412 Vilnius-21, Lithuania
[2]Laboratory of Biomedical Physics, National Cancer Institute, Baublio st. 3b, LT-08660 Vilnius, Lithuania
[3]Biophotonics Group of Laser Research Center, Vilnius University, Saulėtekio ave. 9, LT-10222 Vilnius, Lithuania
*Corresponding author: Email: milda.stan@gmail.com

Abstract

The aim of study was to assess the toxicity and geno-cytotoxicity of CdSe/ZnS-COOH quantum dots (QD) to rainbow trout *Oncorhynchus mykiss* at early stages of development ("eye-egg" stage embryos). Bioassay testing was conducted under controlled laboratory conditions; with a goal of exploring relationship between the duration of exposure to QD and biological effects in exposed fish embryos. Long-term (12-day) tests on fish at early developmental stages were performed under static conditions. QD photoluminescence analysis showed that the outer layer of the egg protects embryos from the penetration and accumulation of QD. The present study indicated that biological effects of QD are related to the structure of chorion. Toxicity study demonstrated that QD did not induce a significant decrease in survival, but induced heart rate changes of embryos during the entire test. Geno-cytotoxicity assay revealed that QD induced micronuclei in erythroblasts of embryos.

Keywords: quantum dots; fish; embryos; toxicity;geno-cytotoxicity

1. INTRODUCTION

The application of nanotechnology in various fields, such as biomedical science and electronics, cosmetic and pharmaceutical industries, is likely going to increase the release of nanoparticles (NP) into the environment in the near future [1]. Therefore, the increasing use of nanotechnologies will lead to significant accumulation of engineered NP into the aquatic organisms [2]. The potential ecotoxicological consequence of NP is a growing concern, but their impact is still poorly characterized [3].

Quantum dots (QD) are small semiconductor NP composed of a semiconductor core, which is often encapsulated by a shell or coated with organic molecules [4]. They are only a few nanometers in diameter (2-10 nm) with great optical properties and are commonly used as fluorophores in vital bioimaging of developmental processes [5]. These properties enable the use of QD *in vitro* and *in vivo* experiments and establish QD as promising tools in disease treatment and targeted therapy. Unfortunately, the limitation of their usage is the toxicity. QD are composed of different metals that may have detrimental effects on the environmental and human health [6].

Several recent review articles dealing with NP toxicity to aquatic organisms focus on NP ecotoxicological potential [1]. The nanocrystal core of many types of QD contains the toxic metal cadmium (Cd), possibly resulting in release of Cd from the QD core [7]. However, QD exerted toxic effects in fish not only due to Cd^{2+} release, but also toxicity that might be associated with QD nanoscale properties [8]. Toxicity, cytotoxicity, mutagenicity, genotoxicity and immunotoxicity in fish exposed to ionic form of Cd have been described. Therefore, high heavy metal content in NP

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makes them potentially harmful to living creatures. In zebrafish, QD induced dose- and age-dependent endpoints of sublethal toxicity, including increased mortality, reduced growth, apparent necrosis, yolk sac malformation, malformed tail and bioaccumulation in body tissues [8-10]. The study by Zhang with co-authors [10] indicated that the mortality increased significantly after zebrafish embryos were exposed to CdTe QD coated with thioglycolic acid. Compared to the CdTe QD, the CdSe/ZnS QD showed lower toxicity in zebrafish embryos and larvae [8, 9]. Blickley with co-authors [11] showed that the chronic QD exposure could cause a negative effect at the population level and maternal transfer of QD or their degradation products to developing progeny may pose a threat to future generations of aquatic organisms. For this reason, QD could be a source of toxicity with fatal impact to fish during the sensitive stages of the embryonic period [11, 9]. Toxicity of different NP (nanosilver, titanium dioxide, silver NPs, single walled carbon nanotubes and QD) on rainbow trout adult was also investigated [12-15, 2]. Knowledge of possible effects in fish embryonic development is still being acquired and could present as valuable information on the QD environmental impact.

The scientific information on the NP toxicity mechanism at early life stages of fish is very limited, especially under varying environmental conditions [3, 7]. Furthermore, there are many factors, which could influence the toxicity of NP in embryos. For example, chemical composition, particle size, shape, surface modification, concentration of particles, crystal form and degree of agglomeration can influence bioaccumulation and the biological effects during embryogenesis [4].

The micronucleus assay is one of the most frequently used tools for the NP genotoxicity assessment [4]. The *in vivo* micronucleus test in fish early life stages were applied in several studies [16-18]. Micronucleus and erythroblast nuclear abnormalities assays previously were used as biomarkers to assess genotoxicity and cytotoxicity of different NP in fish [19, 2]. As emphasized by Rocha with co-authors [20] cytotoxicity and genotoxicity effects of Cd-based QD in aquatic species need to be comprehensively investigated. *In vitro* or *in vivo* chromosome abnormalities, DNA fragmentation induced by CdSe/ZnS core/shell QD have been previously shown in various organisms [21, 22]. Munari with co-authors [2] investigated genotoxicity and cytotoxicity of CdS QD and silver sulphide (Ag_2S) coated with methyl polyethylene glycol in a rainbow trout cell line RTG-2. The results showed that CdS QD was highly cytotoxic at high concentrations, and demonstrated concentration-dependent genotoxicity response in the sub-toxic range after 24 h exposure.

Recently, an expanding number of studies have focused on embryonic stages; however, the comparison between these experiments is difficult as different species of fish, various types of NP, their sizes, concentrations, exposure durations were tested [4]. To the best of our knowledge, there has been no report of using rainbow trout *Oncorhynchus mykiss* embryos as a model for QD long-term toxicity and geno-cytotoxicity studies. It should be noted that this experimental study was done at equal laboratory conditions. Little is known about geno-cytotoxicity effects of QD at early developmental stages of fish in an exposure duration-dependent manner. It is also very important to determine the penetration abilities of QD through the egg envelope that would help to explain QD toxic effects on embryos of various organisms.

The aims of the present study were: (i) to determine the penetration abilities of QD through the egg envelope, (ii) to assess the toxicity and geno-cytotoxicity of QD using the test fish, rainbow trout, in early stages of development – “eye-egg” stage embryos and (iii) to define the relationship between the duration of QD exposure and biological alterations in exposed fish embryos.

2. MATERIALS AND METHODS

Exposure of fish was performed at the Laboratory of Ecology and Physiology of Hydrobionts (Nature Research Centre, Lithuania). Rainbow trout *Oncorhynchus mykiss* eggs (“eye-egg” stage

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embryos) were obtained from the Simnas hatchery (Lithuania). Studies have been carried out with non-protected life-stages accordance with EU Directive 2010/63/EU. The laboratory treatment was carried out in climatic camera (Bronson PGC-660, Germany) under static conditions.

Deep well water of high quality was used for storing control embryos [23]. The average hardness of dilution water was approximately 284 mg L^{-1} as $CaCO_3$, alkalinity was 244 mg L^{-1} as HCO_3^-, the mean pH was 8.0, temperature was maintained at 10 ± 0.5°C, and the oxygen concentration ranged from 8 to 10 mg L^{-1}. Dissolved oxygen in the tanks, temperature and pH were measured routinely with a hand-held multi-meter (WTW Multi 340i/SET, Germany).

Long-term (12-day) toxicity test of QD was conducted using “eye-egg” stage embryos (starting from “eye-egg” embryos 12-day before hatching). The effect of QD on the biological parameters: survival (%) (N = 39 in the control group; N = 38 in the QD group) and heart rate (HR, counts/min) of embryos were recorded. HR of embryos was measured during 1-minute periods for each embryo individually, and the mean value for 10 embryos was calculated. The unfertilized eggs were removed from the groups. Survival was recorded at 24-hour intervals. Studies with embryos were performed in two replications.

Toxic effects of CdSe core, ZnS shell and carboxyl group terminated QD, abbr. CdSe/ZnS-COOH (QD ITK 625, Life Technologies) were analyzed at sublethal concentration of 4×10^{-9} *M* according to [24]. The volume of 100 µl of stock solution of 8 µM was dissolved in the fish media to achieve final QD concentration of 4×10^{-9} *M*. Fluorescence microscopy was used to visualize QD localization in embryonic tissues in order to determine QD distribution. Embryos were prepared using the standard paraffin embedding technique for microscopical examination. They were fixed in 4% formaldehyde solution for 24 hours and were embedded in paraffin blocks for cutting with the microtome. The unstained slices were used for fluorescence microscopy and they were imaged using Nikon C1si confocal microscope, which is equipped argon ion laser (λ=488 nm). The 500-590 nm band pass filter (represented in green color) was used for autofluorescence detection and 620-720 nm band-pass filter (represented in red color) for QD photoluminescence detection.

Geno-cytotoxicity assay was performed on “eye-egg” stage embryos. Genotoxicity [induction of micronuclei (MN) and nuclear buds (NB)] and cytotoxicity [induction of bi-nucleated (BN) and fragmented-apoptotic (FA) cells] endpoints were analysed in erythroblasts. Blood smears were prepared from whole embryonic body (gently nipped with tweezers): directly smeared on glass slides and air-dried. Smears were fixed in methanol for 10 min. and later were stained with 10% Giemsa solution in phosphate buffer pH = 6.8 for 20 - 40 min. The stained slides were analysed under light microscopes Olympus BX51 at final magnification of 1,000×. Micronuclei (MN) were identified according to the following criteria: (1) round and ovoid-shaped non-refractory particles in the cytoplasm, (2) color and structure similar to chromatin of the main nucleus, (3) diameter of 1/3-1/20 of the main nucleus, (4) particles completely separated from the main nucleus [25]. Identification of nuclear buds, fragmented-apoptotic and bi-nucleated cells was done using criteria described by Fenech with co-authors [26]. The frequencies of abnormalities were recorded in 1,000 erythroblasts per slide using blind scoring by a single observer. The 4-day duration test was carried out with embryos (7 specimens in QD exposed and 7 specimens in control groups) for evaluating geno-cytotoxicity.

Differences between the evaluated characteristics studied were tested by two-way ANOVA at $p < 0.05$ using Statistica 7.0 software’s (USA). Pearson correlation analysis was performed to identify possible relationships between biological parameters of embryos and the duration of exposure. GraphPad Prism 5 (USA) statistical analysis software was used in geno-cytotoxicity statistical analysis. Non-parametric Mann-Whitney *U*-test was used to compare frequencies of nuclear abnormalities observed in embryos from control and exposed groups. Differences were accepted as significant at the 95% level of confidence ($p < 0.05$).

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3. RESULTS

3.1 Incubation of the embryos with QD

Rainbow trout embryos, in early stages of development – "eye-egg" stage were cultivated and exposed to the QD according to the guidelines presented in ISO standard (ISO 7346-1:1996). The formation of aggregates of QD in the incubation water were detected (Figure 1A). However, spectroscopy reveals that QD are stable in the incubation solution. The photoluminescence intensity decay with increasing of the incubation time is related to the aggregation of QD in water and agglomeration on the eggs surface (Figure 1). Confocal fluorescence microscopy was used to visualize QD localization in egg in order to determine QD distribution. QD are covering the envelope of the egg, but they were not observed in the deeper layers. The green color represents the autofluorescence of the embryonic tissues and red color represents the fluorescence of QD (Figure 1B). For rainbow trout embryos, most of the particles were accumulated at the surface of the envelope surrounding the embryos (Figure 1B).

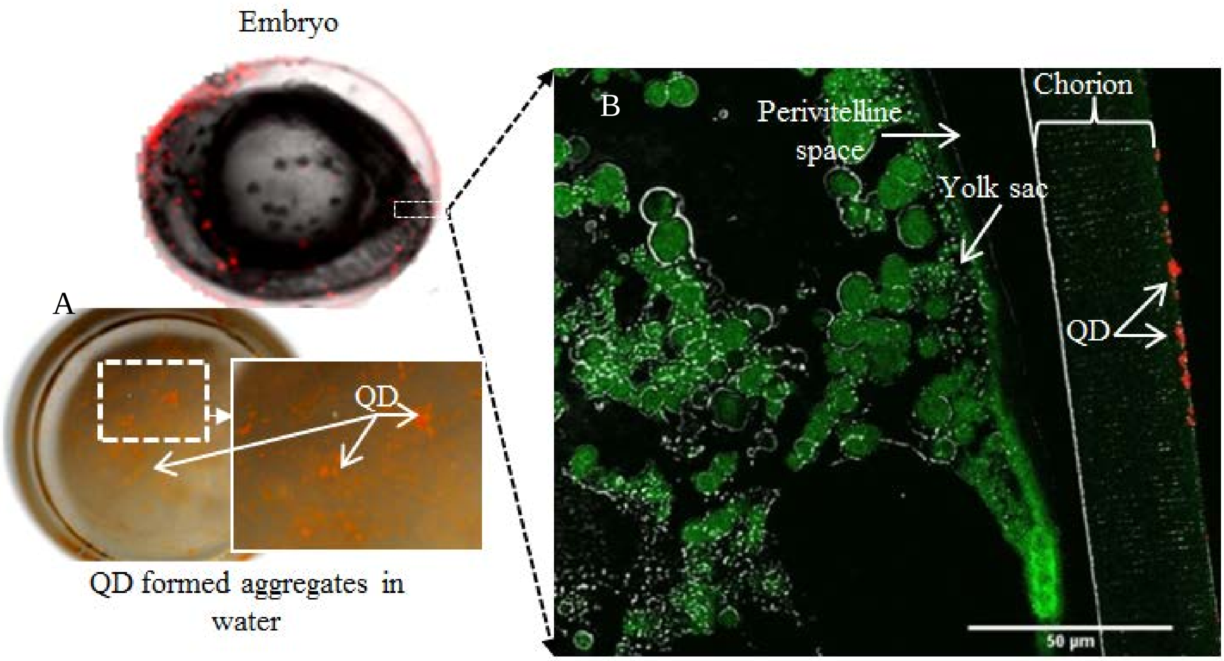


Figure 1. QD formed large aggregates in water (A). Confocal fluorescence microscopy image (B) rainbow trout egg exposed to QD for 8-day. QD (red color) adhere to the envelope but do not penetrate through it to the inner layers of the egg.

3.2 Toxicity

Survival of the embryos exposed to QD during the 1-, 4-, 8-, 12-day of the test did not significantly differ from the survival in control group (Figure 2A). The heart rate (HR) of embryos exposed to QD during the 1-, 4-day was significantly ($p < 0.05$) lower (80.4 ± 4.8; 82.0 ± 4.2 count/min, respectively) as compared to the control (95.2 ± 6.5; 94.8 ± 6.3 count/min, respectively). Meanwhile after 8- and 12-day exposure HR of embryos (89.2 ± 7.4; 90.0± 8.5 counts/ min, respectively) didn't differ significantly from the control (96.0 ± 3.3 counts/min). The alterations in HR of embryos were related to the duration of exposure of QD (Figure 2B). HR of embryos after 1- and 4-day exposure was significantly ($p < 0.05$) different from 12-day exposure. Pearson correlation analysis of HR and the duration of exposure of embryos showed moderate and positive correlations (r = 0.53). It shows that HR is decreased at the day of adding QD to the media, but later it recovers to the level of the control group.

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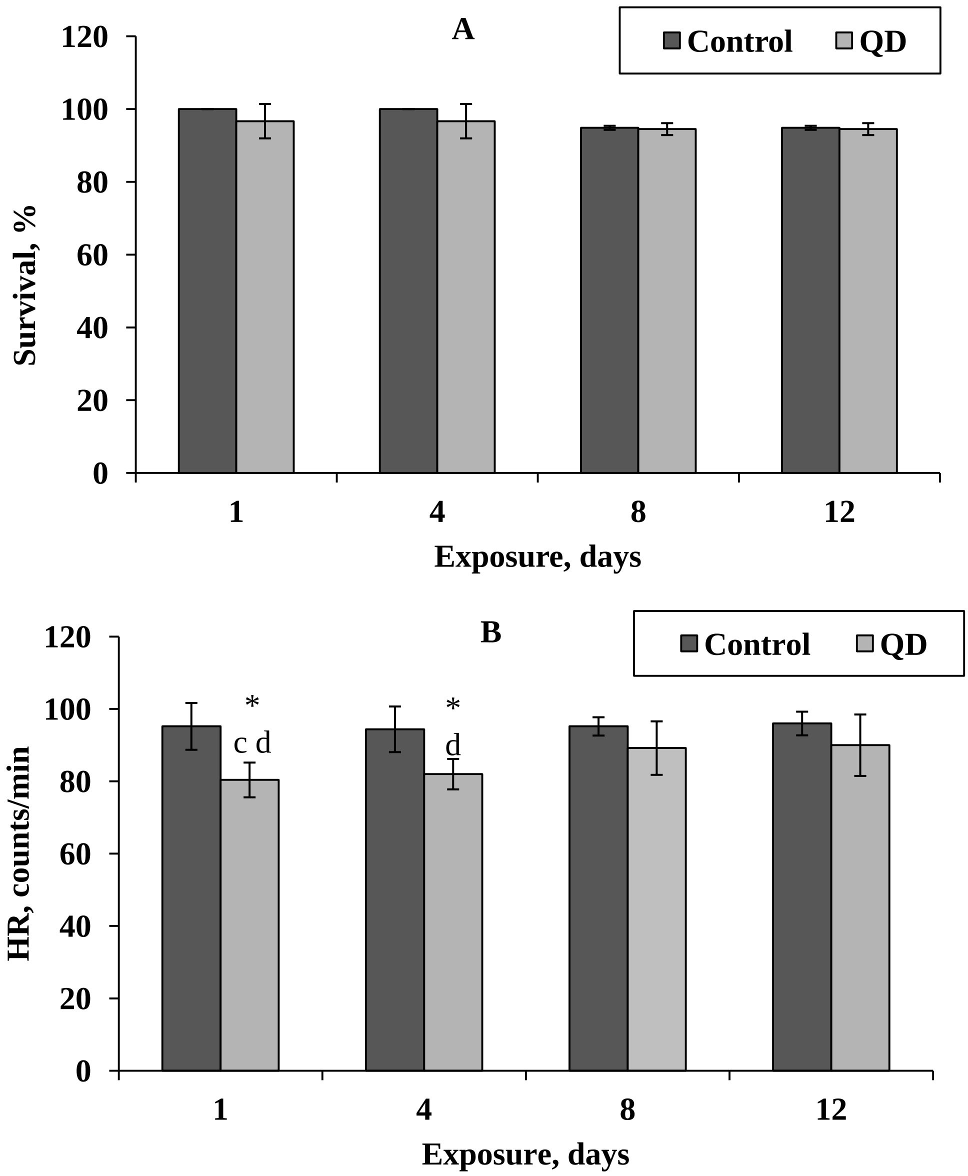


Figure 2. Effect of QD on the survival (A) and the HR (B) of embryos depending on the duration of exposure. Columns and bars represent means ± SD.

* Significantly different from control: $p < 0.05$. Significantly different between the duration of exposure ($p < 0.05$): c- significantly different from the 8-day of exposure; d-significantly different from the 12-day of exposure.

3.3 Geno-cytotoxicity

Exposure (4-day) to QD significantly ($p = 0.044$) increased frequency of micronuclei (MN) in embryos, but did not induced nuclear buds (NB), bi-nucleated and fragmented-apoptotic erythroblasts. However, all analysed geno-cytotoxicity responses were elevated approximately 2 times compared to the control levels (Figure 3). Micronucleated erythroblast, erythroblast with nuclear bud, bi-nucleated and fragmented-apoptotic erythroblast in embryos exposed to QD are presented in Figure 4.

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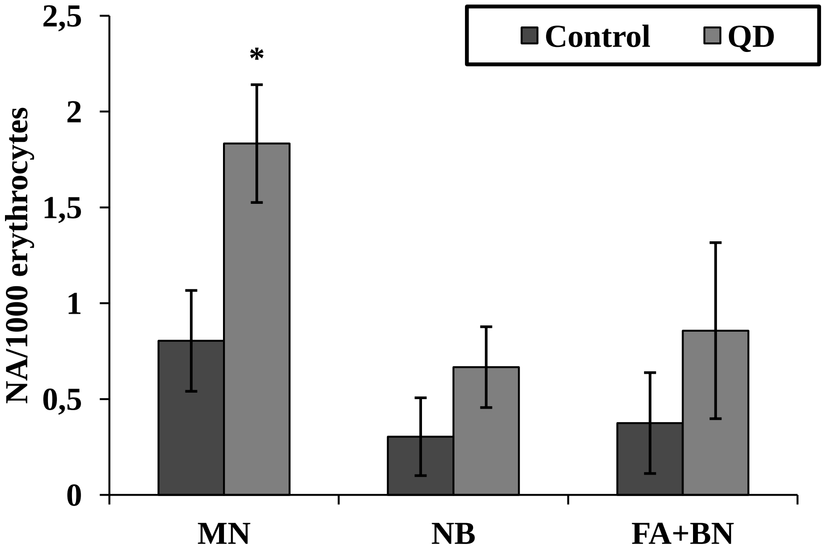


Figure 3. Frequency of micronuclei, nuclear buds and fragmented-apoptotic (FA) + bi-nucleated (BN) erythroblasts of embryos exposed 4-day to QD. Data are reported as mean ± SE. Differences between control and exposure groups shown: * $p \leq 0.05$.

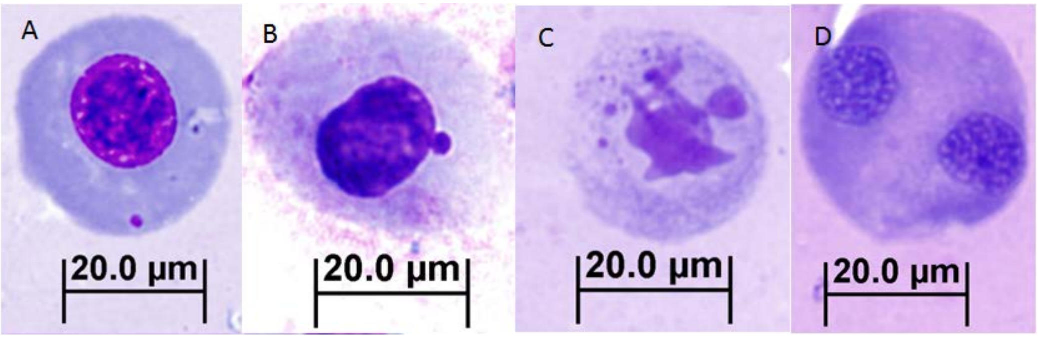


Figure 4. Rainbow trout embryo erythroblast with (A) micronucleus (MN), (B) nuclear bud (NB), (C) fragmented-apoptotic (FA) and (D) bi-nucleated (BN) erythroblast.

4. DISCUSSION

Our results showed that QD formed large aggregates in water (Figure 1 A). QD adhere to the envelope but do not penetrate through in to the inner layers of the rainbow trout egg (Figure 1 B). For this reason, QD did not penetrated the chorion of embryo but QD aggregates affected the ability of larval fish to hatch [8, 11]. These results are also supported by our observations obtained using the confocal microscope. QD adhered to the envelope but did not penetrate through it to the inner layers of the egg [24]. Similar results were observed when photoluminescence SiO_2 nanoparticles (~60 and ~200 nm in diameter) were exposed to zebrafish embryos; the nanoparticles adhered to the surface of the chorion but did not enter the embryo [27]. Exposure of *Fundulus heteroclitus* embryos to aqua-nC60 resulted in very little mortality and aggregates adhered to the chorion, not affecting development of the embryos or their hatching success [11].

Our data showed that survival of rainbow trout embryos exposed to QD in long-term tests remained statistically unchanged (Figure 2A). According to King-Heiden with co-authors [8] coating or size of QD can influence the embryonic toxicity, as it was shown in case of CdSe/ZnS QD coated with PEG or polylysine in zebrafish embryos. QD induced higher mortality than the

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equivalent amount of Cd^{2+}, probably due to the specific organic coating, QD scale or degree of their agglomeration in solution [8]. But there is another opinion to interpret the toxicity of QD. Because of a lack of protection of the egg membrane, a large amount of water- soluble Cd likely penetrated into the embryos and accumulated around the eggs, especially at high concentrations, and finally led to death [28]. However, interestingly chorion of various fish species may differentially retain Cd. For example, in rainbow trout (*Oncorhynchus mykiss*) 98 % of total Cd was retained by chorion, meanwhile, 61 % in zebrafish (*Danio rerio*) [28]. Annabi with co-authors [28] provided the evidence of the protective effect of the chorion and showed that hatched larvae are more susceptible to Cd than unhatched embryos [28]. Meanwhile, rainbow trout embryos during hatching are more sensitive to external substances at the early stages rather than larval or adult stages [29].

Effects of NP on early life stages of fish are emerging, with reports of crossing the chorion (e.g., Ag-NPs) [29]. The evidence on the protective effect of the chorion (a membrane envelope surrounding the egg) suggested that it acts as a barrier to Cd transfer to the developing embryos [32].

Table 1 Chorion thickness and total Cd was retained by chorion of various fish species (Literature review)

Fish species	Chorion thickness/ Total Cd was retained by chorion	Authors
Fundulus heteroclitus	13 μm	[31]
Oryzias latipes	12-15 μm/ 94.6%	[32]/[28]
Danio rerio	0.5-0.6 μm/ 61 %	[33]/[28]
Oncorhynchus mykiss	44.2-48.6 μm/ 98 %	[34]/[28]

According to Ninness with co-authors [35], the majority of fish embryos develop surrounded by a fluid layer known as the perivitelline fluid encased in a tough acellular shell or chorion that is composed mainly of protein and glycoprotein. One of the major functions of the chorion is to physically and chemically protect and isolate the embryo from external environmental conditions/impacts. In addition, the chorion is involved in respiration, excretion of metabolic waste and ionic and osmotic balance. In Table 1 the chorion thickness of various fish species are presented. According to Berois with co-authors [36], there are numerous channels cross the entire width of the chorion in a regular pattern. The main focus in Henn's [37] work has been to determine the influence of the chorion on chemical toxicity for zebrafish embryos.

Meanwhile, the exposure to QD induced significant decrease in HR of embryos in relation to the duration of exposure (r = 0.53) (Figure 2B). Interestingly the HR of embryos exposed to QD for 1-, 4-day, was significantly ($p < 0.05$) lower as compared to the control. However, at the later time the HR recovers to the normal levels.

This indicates the possibility of acclimation to QD effect. Meanwhile, little is known about acclimation mechanisms in early developmental stages of fish. Possibility of acclimation of larvae of *Salmo trutta* and *Pimephales promelas* by exposure to Cd were observed [38]. According to Jezierska with co-authors [39] the increase in HR during development might have been related to the observed increase in embryonic activity and is an indicator of metabolic rate in embryos. A decrease in HR during hatching period was particularly pronounced in metal-exposed embryos [39]. Wang with co-authors [40] hypothesized that the accumulation of the QD occurs in the zebrafish heart and the substance provokes malformed heart. This is confirmed and by other authors [8, 9].

The clastogenic/aneugenic properties of CdSe/ZnS QD have been observed in some studies [21, 22]. Galeone with co-author [22] suggested classifying CdSe/ZnS QD as significantly toxic in

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long-term *in vivo* treatments. Nanoparticle-induced oxidative stress is thought to be a key mechanism responsible for genotoxicity effects [41]. Brunetti with co-authors [42] reported Cd^{2+} ions leaching from the CdSe core despite the two-layer ZnS shell. Furthermore, a coating-dependent reactive oxygen species (ROS) generation of CdSe/ZnS core/shell QD was emphasized by Galeone and co-authors [22]. Several studies have pointed to PEG-coating that can protect from Cd^{2+} leak. It was concluded that coating with PEG decreases toxicity, but does not eliminate it [43, 22]. Zhang with co-authors [44] emphasized that PEG-coated silanized QD causes minimal impact to cells. Saez with co-author [45] showed that genotoxicity potential and reactivity of Cd with intracellular targets are influenced by its nano or ionic form. Nano-Cd showed a stronger genotoxic activity compared with ionic-Cd in *Hediste diversicolor*. However, Aye's and co-authors' [21] results showed, that even though QD induced ROS, the mutagenic/clastogenic properties of QD are not completely accounted for. The inherent physico-chemical properties of QD may generate various reactions, which results in genotoxicity/mutagenicity effects in cells or organisms. Other possible mechanisms underlying genotoxicity of QD are inflammation, aberrant signaling responses and direct interaction with DNA and nuclear proteins [42]. Thus, potential for genotoxicity effects and mechanisms of DNA damage of QD still remains unclear [45].

Heavy metal embryonic uptake is known to be blocked by the chorion via binding, most likely via complexation by anionic charged groups, possibly thiol-groups, which are abundantly present in the chorion [37]. Furthermore, it was suspected, that the chorion pores potentially restrict the uptake of compounds depending on their size [37]. In addition, NP cause increased mucus production in fish, may thicken the mucus layer and impair gas exchange [46]. Our results showed significantly increased frequencies of MN, slight increase of other nuclear abnormalities and reduced HR after QD exposure. However, fluorescence microscopy showed that QD accumulation is visible around the outer layer of the egg; indicating the QD did not penetrate the chorion and were not observed in the embryo. More follow-up studies must provide information, which mechanism: Cd leakage or QD adhesion to the envelope of the egg and thus possible disruption of gas exchange is responsible for toxicity and genotoxicity. Therefore, the long-term fish exposure to QD requires further detailed toxicological analysis.

In the present study, the toxicity and geno-cytotoxicity of QD were assessed using rainbow trout embryos as test organism. The toxicity and geno-cytotoxicity of QD and their effect on embryonic survival, physiological parameters such as HR, induction of micronucleus, penetration abilities can provoke developmental defects of fish in larvae or adult stages. The nanocrystal core of CdSe/ZnS-COOH QD contains the toxic metal Cd, thus possible release of Cd from the QD core could contribute to the effects seen. The long-term study of QD toxicity and geno-cytotoxicity effects on embryos should provide new information for understanding QD impact mechanisms. The laboratory-controlled assessment of toxicity and geno-cytotoxicity effects on embryos of rainbow trout reported here provides new information about environmental risk of the QD and opens new avenues for investigating the emerging effects of QD.

5. CONCLUSIONS

CdSe/ZnS-COOH QD does not cause embryonic survival of rainbow trout at the dose of 4×10^{-9} *M* up to 12 days. QD exposure causes the decrease of the HR in the first 4 days of exposure, but this effect is later compensated and restored to a normal level. Exposure to QD causes genotoxicity (increased the frequency of micronuclei in erythroblasts) in embryos. The outer layer of the egg protects embryo from the penetration and accumulation of QD.

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References

[1] Jovanovic, B., 2011. Immunotoxicology of titanium dioxide and hydroxylated fullerenes engineered nanoparticles in fish models. *Graduate Theses and Dissertations*, 10134.

[2] Munari, M., Sturve, J., Frenzilli, G., Sanders, M. B., Brunelli, A., Marcomini, A., Nigro, M., Lyons, B. P., 2014. Genotoxic effects of CdS quantum dots and Ag_2S nanoparticles in fish cell lines (RTG-2). *Mutation Research - Genetic Toxicology and Environmental Mutagenesis*, **16 (775–776)**, 89–93.

[3] Kim, J., Park, Y., Yoon, T. H., Yoon, Ch. S., Choi, K., 2010. Phototoxicity of CdSe/ZnSe quantum dots with surface coatings of 3-mercaptopropionic acid or tri-n-octylphosphine oxide/gum arabic in *Daphnia magna* under environmentally relevant UV-B light. *Aquatic Toxicology*, **97 (2)**, 116–124.

[4] Celá, P., Veselá, B., Matalová, E., Večeřa, Z., Buchtová, M., 2014. Embryonic Toxicity of Nanoparticles. *Cells Tissues Organs*, **199 (1)**, 1–23.

[5] Michalet, X., Pinaud, F.F., Bentolila, L.A., Tsay, J.M., Doose, S., Li, J.J., Sundaresan G.,Wu, A.M., Gambhir, S.S.,Weiss, S., 2005. Quantum dots for live cells, in vivo imaging, and diagnostics. *Science*, **307 (5709)**, 538–544.

[6] Blažková, I., Konečná, M., Kenšová, R., Adama, V., Kizeka, R., 2014. Application of quantum dots into chicken embryos. *Journal of Metallomics and Nanotechnologies*, **3**, 26–28.

[7] Leigh, K.L., Bouldin, J.L., Buchanan, R.A., 2014. Measurement of Accumulation of Semiconductor Nanocrystal Quantum Dots by *Pimephales Promelas*. *Dose-Response: An International Journal*, **10 (3)**, 331–334.

[8] King-Heiden, T. C., Wiecinski, P. N., Mangham, A. N., Met, K. M., Nesbit, D., Pedersen, J.A., Hamers, R. J., Heideman, W., Peterson, R. E., 2009. Quantum dot nanotoxicity assessment using the zebrafish embryo. *Environmental Science & Technology*, **43 (5)**, 1605–1611.

[9] Duan, J., Yu, Y., Li, Y., Yu, Y., Li, Y., Huang, P., Zhou, X., Peng, S., Sun, Z., 2013. Developmental toxicity of CdTe QDs in zebrafish embryos and larvae. *Journal of Nanoparticle Research*, **15**:1700.

[10] Zhang, W., Lin, K., Miao, Y., Dong, Q., Huang, C., Wang, H., Guo, M., Cui, X., 2012. Toxicity assessment of zebrafish following exposure to CdTe QDs. *Journal of Hazardous Materials*, **213–214**, 413–420.

[11] Blickley, T. M., Matson, C., W., Vreeland, W. N., Rittschof, D., Di Giulio, R. T., McClellan-Green, P., D., 2014. Dietary CdSe/ZnS quantum dot exposure in estuarine fish: Bioavailability, oxidative stress responses, reproduction, and maternal transfer. *Aquatic Toxicology*, **148**, 27–39.

[12] Federici, G., Shaw, B.J, Handy, R.D., 2007. Toxicity of titanium dioxide nanoparticles to rainbow trout (*Oncorhynchus mykiss*): gill injury, oxidative stress, and other physiological effects. *Aquatic Toxicology*, **84 (4)**, 415–430.

[13] Smith, C.J., Shaw, B.J., Handy, R.D., 2007. Toxicity of single walled carbon nanotubes to rainbow trout, (*Oncorhynchus mykiss*): respiratory toxicity, organ pathologies, and other physiological effects. *Aquatic Toxicology*, **82 (2)**, 94–109.

[14] Shahbazzadeh, D., Ahari, H., Rahimi, N.M., Dastmalchi, F., Soltani, M., Fotovat, M., Rahmannya, J., Khorasani, N., 2009. The Effects of Nanosilver (Nanocid®) on Survival Percentage of Rainbow Trout (*Oncorhynchus mykiss*). *Pakistan Journal of Nutrition*, **8 (8)**, 1178–1179.

[15] Scown, T.M., Santos, E.M., Johnston, B.D., Gaiser, B., Baalousha, M., Mitov, S., Lead, J.R., Stone, V., Fernandes, T.F., Jepson, M., van Aerle, R., Tyler, C.R., 2010. Effects of aqueous exposure to silver nanoparticles of different sizes in rainbow trout. *Toxicological Sciences*, **115 (2)**, 521–534.

[16] Hayashi, M., Ueda, T., Uyeno K., Wada, K., Kinae, N., Saotome, K., Tanaka, N., Takai, A., Sasaki, Y.F., Asano, N., Sofuni, T., Ojima, Y., 1998. Development of genotoxicity assay systems that use aquatic organisms. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis*, **399 (2)**, 125–133.

[17] Braunbeck, T., Böttcher, M., Hollert, H., Kosmehl, T., Lammer, E., Leist, E., Rudolf, M., Seitz, N., 2005. Towards an Alternative for the Acute Fish LC50 Test in Chemical Assessment: The Fish Embryo Toxicity Test Goes Multi-species – an Update. *Alternatives to Animal Experiments*, **22 (2)**, 87–102.

ISBN: 978-960-6865-94-7

[18] Le Bihanic, F., Clérandeau, C., Le Menach, K., Morin, B., Budzinski, H., Cousin, X., Cachot, J., 2014. Developmental toxicity of PAH mixtures in fish early life stages. Part II: adverse effects in Japanese medaka. *Environmental science and pollution research international*, **21 (24)**, 13732–13743.
[19] Vignardi, C.P., Hasue, F.M., Sartório, P.V., Cardoso, C.M., Machado, A.S., Passos, M.J., Santos, T.C., Nucci, J.M., Hewer, T.L., Watanabe, I.S., Gomes, V., Phan, N.V., 2015. Genotoxicity, potential cytotoxicity and cell uptake of titanium dioxide nanoparticles in the marine fish *Trachinotus carolinus* (Linnaeus, 1766). *Aquatic Toxicology*, **158**, 218–229.
[20] Rocha, T.L., Gomes, T., Cardoso, C., Letendre, J., Pinheiro, J.P., Sousa, V.S., Teixeira, M.R., Bebianno, M.J., 2014. Immunocytotoxicity, cytogenotoxicity and genotoxicity of cadmium based quantum dots in the marine mussel *Mytilus galloprovincialis*. *Marine Environmental Research,* **101**, 29–37.
[21] Aye, M., Di Giorgio, C., Berque-Bestel, I., Aime, A., Pichon, B.P., Jammes, Y., Barthélémy, P., De Méo, M.. 2013. Genotoxic and mutagenic effects of lipid-coated CdSe/ZnS quantum dots. *Mutation Research*. **750 (1 – 2)**, 129–138.
[22] Galeone, A., Vecchio, G., Malvindi, M.A., Brunetti, V., Cingolani, R., Pompa, P.P., 2012. In vivo assessment of CdSe-ZnS quantum dots: coating dependent bioaccumulation and genotoxicity. *Nanoscale*, **4**, 6401–6407.
[23] Svecevičius, G., 2010. Acute toxicity of nickel to five species of freshwater fish. *Polish Journal of Environmental Studies*, **19 (2)**, 453–456.
[24] Cibulskaitė, Ž., Kazlauskienė, N., Kulvietis, V., 2015. Sublethal toxicity of quantum dots and heavy metals *to* rainbow trout (*Oncorhynchus mykiss*) in early ontogenesis. Proceedings of the 18th Conference for Junior Researchers „Science – Future of Lithuania“, *Environmental protection engineering.* 9 April 2015, Vilnius, Lithuania, 31–37.
[25] Heddle, J.A., Cimino, M.C., Hayashi, M., Romagna, F., Shelby, M.D., Tucker, J.D., Vanparys, P., MacGregor, J.T., 1991. Micronuclei as an index of cytogenetic damage: past, present, and future. *Environmental and Molecular Mutagenesis*, **18 (4)**, 277–291.
[26] Fenech, M., Chang, W.P., Kirsch-Volders, M., Holland, N., Bonassi, S., Zeiger, E., 2003. HUMN project: detailed description of the scoring criteria for the cytokinesis-block micronucleus assay using isolated humanlymphocyte cultures. *Mutation Research*, **534**, 65–75.
[27] Sun, J., Zhang, Q., Wang, Z. and Yan B., 2013. Effects of Nanotoxicity on Female Reproductivity and Fetal Development in Animal Models. *International Journal of Molecular Sciences*, **14**, 9319–9337.
[28] Annabi, A., Said, K., Messaoudi, I., 2013. Cadmium: Toxic Effects and Physiological Impairments in Fishes. *International Journal of Advanced Research*, **1 (3)**, 372–382.
[29] Vosylienė, M. Z., Kazlauskienė, N., Svecevičius, G., 2003. Effect of heavy metal model mixture on biological parameters of rainbow trout *Oncorhynchus mykiss*. *Environmental Science* & *Pollution Research.* **10**, 103–107.
[30] Shaw, B.J., Handy, R.D., 2011. Physiological effects of nanoparticles on fish: a comparison of nanometals versus metal ions. *Environment International*, **37 (6)**, 1083–1097.
[31] Shanklin, D.R., 1959. Studies on the Fundulus chorion. *Journal of Cellular and Comparative Physiology*, **53**, 1–11.
[32] Hart, N.H., Pietri, R., Donovan, M., 1984. The structure of the chorion and associated surface filaments in Oryzias – evidence for the presence of extracellular tubules. *Journal of Experimental Zoology*, **230**, 273–296.
[33] Joo, K.B., Kim, D.H., 2013. Comparative ultrastructures of the fertilized egg envelopes in *Danio rerio* and *Danio rerio* var. frankei, *Cyprinidae*, Teleostei. *Applied Microbiology*, **4**3, 14–20.
[34] Lahnsteiner, F., 2000. Morphological, physiological and biochemical parameters characterizing the over-ripening of rainbow trout eggs. *Fish Physiology and Biochemistry,* **23**, 107–118.
[35] Ninness, M.M., Don Stevens, E., Wright, P. A., 2006. Removal of the chorion before hatching results in increased movement and accelerated growth in rainbow trout (*Oncorhynchus mykiss*) embryos. *The Journal of Experimental Biology*, **209**, 1874–1882.
[36] Berois, N., Arezo, M.J., Papa, N.G., 2011. Gamete interactions in teleost fish: the egg envelope. Basic studies and perspectives as environmental biomonitor. *Biological Research,* **44 (2)**, 119–124.
[37] Henn, K., 2011. Limits of the fish embryo toxicity test with Danio rerio as an alternative to the acute fish toxicity test. Dissertation for the degree of Doctor, Ruperto-Carola University of Heidelberg, Germany.
[38] Witeska M., Sarnowski P., Ługowska K., and Kowal E., 2014. The effects of cadmium and copper on embryonic and larval development of ide *Leuciscus idus* L. *Fish Physiology and Biochemistry.* **40 (1)**, 151–163.
[39] Jezierska, B., £ugowska, K., Witeska, M., 2002. The effect of temperature and heavy metals on heart rate changes in common carp *Cyprinus carpio* L. and grass carp *Ctenopharyngodon idella* (Val.) during embryonic development. *Archives of Polish Fisheries*, **10 (2)**, 153–165.
[40] Wang, Z.G., Zhou, R., Jiang, D., Song, J.E., Xu, Q.,Si, J.,Chen, Y.P., Zhou, X., Gan, L., Li, J.Z., Zhang, H.,Liu, B., 2015. Toxicity of Graphene Quantum Dots in Zebrafish Embryo. *Biomedical and Environmental Sciences*, **28 (5)**, 341–351.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[41] Singh, N., Manshian, B., Jenkins, G.J., Griffiths, S.M., Williams, P.M., Maffeis, T.G., Wright, C.J., Doak, S.H., 2009. NanoGenotoxicology: the DNA damaging potential of engineered nanomaterials. *Biomaterials*, **30 (23–24)**, 3891–3914.

[42] Brunetti, V., Chibli, H., Fiammengo, R., Galeone, A., Malvindi, M.A., Vecchio, G., Cingolani, R., Nadeau, J.L., Pompa, P.P., 2013. InP/ZnS as a safer alternative to CdSe/ZnS core/shell quantum dots: *in vitro* and *in vivo* toxicity assessment. *Nanoscale*, **5 (1)**, 307–317.

[43] Ju, Li., Zhang, G., Zhang, C., Sun, Li., Jiang, Y., Yan, C., Duerksen-Hughes, P.J., Zhang, X., Zhu, X., Chen, F.F., Jun, Yang, 2013. Quantum dot-related genotoxicity perturbation can be attenuated by PEG encapsulation. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, **753 (1)**, 54–64.

[44] Zhang, T., Stilwell, J.L., Gerion, D., Ding, L., Elboudwarej, O., Cooke, P.A., Gray, J.W., Alivisatos, A.P., Chen, F.F., 2006. Cellular effect of high doses of silica-coated quantum dot profiled with high throughput gene expression analysis and high content cellomics measurements. *Nano Letters*, **6 (4)**, 800–808.

[45] Saez, G., Aye, M., De Meo, M., Aimé, A., Bestel, I., Barthélémy, P., Di Giorgio, C., 2015. Genotoxic and oxidative responses in coelomocytes of Eisenia fetida and Hediste diversicolor exposed to lipid-coated CdSe/ZnS quantum dots and $CdCl_2$. *Environmental Toxicology*, **30 (8)**, 918–926.

[46] Villarreal, F.D., Das, G.K., Abid, A., Kennedy, I.M., Kültz, D., 2014. Sublethal effects of CuO nanoparticles on Mozambique tilapia (*Oreochromis mossambicus*) are modulated by environmental salinity. *PLoS One*, **9 (2)**, e88723.

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Influence of newly synthesized Cu(II) complexes on the pyrazole based derivatives on inhibition of *Phomopsis viticola* (Sacc.) Sacc.

Z. K. Jacimovic[1*], I. Bošković[1], A. Radović[2], M. Kosović[1], N. Latinovic[3]

[1] University of Montenegro, Faculty of Metallurgy and Technology, Dordža Vašingtona bb, Podgorica, Montenegro
[2] Accreditation body of Montenegro, Džordža Vasingtona 51, Podgorica
[3] University of Montenegro, Biotechnical Faculty, Mihaila Lalića , Podgorica, Montenegro
*Corresponding author: Email: zeljkoj@ac.me

Abstract

Widely spread disease of grapevine caused by fungi *Phomopsis viticola* (Sacc.) has provoked initiation of multidisciplinary research in Montenegro. Based on the fact that the pyrazoles, as fungicide active ingredient, have shown practical application in the protection of fruit trees and taking into account available data on the biochemical role of copper in the ecosystems, the synthesis of new copper (II) complex with selected pyrazole derivative formula: $Cu(L\text{-}H)_2(H_2O)_2$ (L- 1,3-dimethyl-1H-pyrazole-5-carboxylic acid) following method , then its structural characterization and finally determination of the biological effects of Cu(II)complex on *Ph. viticola* has been performed. In order to determine the biological effect of newly synthesized Cu(II)complex, five samples of fungicide Cabrio top (whose active ingredient pyraclostrobin belongs to pyrazole derivatives) with the range of concentrations (3.09– 0.19 mmol dm^{-3}) and also five samples of newly synthesized Cu(II)complex with concentration range (1.78- 0.11 mmol dm^{-3}) have been prepared. By analyzing statistical results obtained from biological research it is noted that all concentrations of mentioned range of Cabrio top and newly synthesized Cu(II)complex showed a significant inhibitory effect on *Ph. viticola* comparing to the control sample

Keywords: pyrazole; newly synthesized Cu(II)complex; active component of fungicide; Phomopsis viticola (Sacc.) Sacc.

1. INTRODUCTION

Pyrazole based compounds and their transition metal complexes have attracted considerable research interest because of potentially beneficial biological properties [1,2]. Starting from the practical applications of pyrazole derivatives, as active ingredients in fungicides [3] existing Cu compounds for the protection of the grapevine [4], this paper presents a method of synthesis of $Cu(L\text{-}H)_2(H_2O)_2$ complex , where is L= 1,3-dimethyl-1H-pyrazole-5-carboxylic acid, and its determines its inhibiting effect on the mycelium *Ph. viticola* the cause of decay of grapevine in Montenegro. Figure 1. presents symptoms of decay in grapevine.



Figure 1. Symptoms of decay in grapevine (photo: N. Latinović)

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The structure of ligand (L=1,3-dimethyl-1H-pyrazole-5-carboxylic acid) is presented in Figure 2.

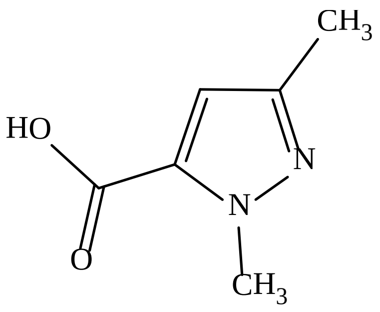


Figure 2. Structure of pyrazole derivate L = 1,3-dimethyl-1H-pyrazole-5-carboxylic acid

1.1 Fungicide Cabrio top

With an aim to achieve a representative selection of the standard for determining biological efficiency (the inhibition effects) newly synthesized Cu (II) complex, the commercial fungicide selected Cabrio Top (fungicide used for the prevention of major diseases of grapevine) [5], which contains pyraclostrobin, (methyl(αE)-2-[[[3-(4-chlorophenyl)-1-methyl-1H-pyrazol-5-yl]oxy] methyl]-α-(methoxymethylene) benzeneacet, belongs to pyrazole derivates, was selected. (Figure 3.)

It is important to note that other active substances of Cabrio top is metiram (Zinc ammonium ethylenebis (dithiocarbamate) poly (disulfide) ethylenethiuram) which belongs to the dithiocarbamate class of fungicides such as mancozeb, a fungicide used in previous studies [4].

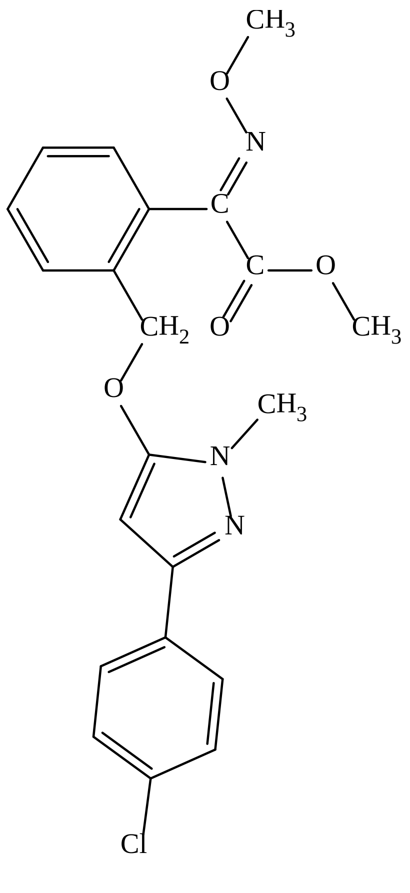


Figure 3. Structure of piraklostrobin

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2. MATERIALS AND METHODS

2.1 Synthesis of Cu (II) complex

A warm methanolic solution of the ligand (8mL) $C_6H_8N_2O_2$ (0.5 mmol) was mixed with a warm methanolic solution (8mL) salt $Cu(CH_3COO)_2 \cdot H_2O$ (0.25 mmol). After two days the blue single crystal product was filtered off and washed with methanol. Yield was 84,29% (0,080g).
For this synthesis, 1,3-Dimethyl-pyrazole-5-carboxylic acid was used as purchased from Sigma-Aldrich.

2.2. Crystal structures

The crystal structure of $Cu(L\text{-}H)_2(H_2O)_2$ complex has been determined by single-crystal X-ray diffraction. The complex crystallizes in space group $P2_1/c$. The Cu atom is placed in nearly ideal square planar environment formed by pairs of oxygen donors from the deprotonated carboxylic acid and H_2O molecules. The presence of a methyl substituent on the N^1 atom of HL prevents bidentate coordination common for pyrazole-5-carboxylic acid based ligand, therefore in Cu(II) complex the ligand is monodentatly coordinated to the metal ion (Figure 4.). The crystal structures of complexe are stabilized by extensive O−H…O and O−H…N hydrogen bonds, where H_2O and methanol ligands play a significant role as hydrogen bonding donors [6].

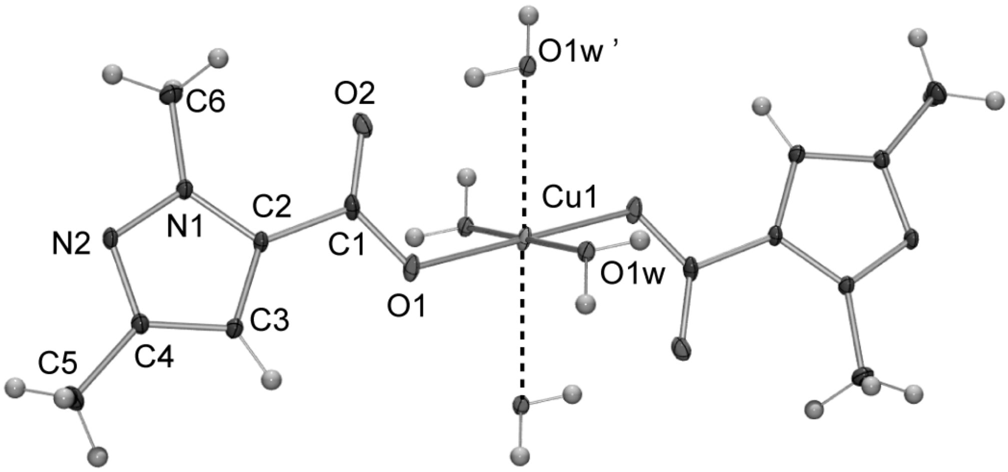


Figure 4. Molecular structure of $Cu(L\text{-}H)_2(H_2O)_2$

Crystallographic data of the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 1015253. The data are available free of charg**e *via* www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge** CB2 1EZ, UK; +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

2.3 Biological research

Biological research based on determining the inhibition effect of commercial fungicide Cabrio top and newly synthesized Cu(II) complex on *Ph. viticola* have been carried using the phytosanitary method at the laboratory of Center for plant protection of the Biotechnical Faculty University of Montenegro. The diameters of fungal mycelium Ph. Vitiocola as parameters of the inhibition effect of the prepared samples of commercial fungicide Cabrio top and newly synthesized $Cu[L\text{-}H]_2(H_2O)_2$ complex were processed using the variance analysis, while the testing was done using the LSD test [7].

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2.4 Method of preparate of sample of Cabrio top and newly synthesized $Cu[L-H]_2 (H_2O)_2$ complex for biological research

Prepared by $20cm^3$ solution selected sample of Cabrio top (initial mass 0.04g) and 0.0134g newly synthesized $Cu[L-H]_2 (H_2O)_2$ complex.

Then carried out a double dilution of each of the previous solution in 4 repetitions for the determination of the biological efficacy of the inhibition of mycelium of *Ph. viticola*. The solutions were prepared as described above and then they were entered into the nutrient medium (PDA) at a ratio of 10:1. A clip of fungus *Ph. Viticola* was placed on the substrate and left in a thermostat at 25°C for two days, when it was committed, and the measurement of the diameter of formed of mycelium a control sample was also assessed.

3. RESULTS AND DISCUSSION

In the study presented here, the newly synthesized $Cu[L-H]_2 (H_2O)_2$ complex has been subjected to tests of mycelia growth inhibition by *Ph. viticola* and shown certain inhibition with regard to control. Results of the antifugal activity tests are summarized in Table 1 and Table 2. Obtained results on the efficacy of Cu(II) complex compered and analyzed based on the LSD test (least significant difference test). Each time the complex was tested for its ability to inhibit mycelia growth of *Ph. viticola,* an analogue experiment with Cabrio top was set up.

Table 1. Inhibition effect of Cabrio Top against the fungal mycelium *Ph. viticola*

Concentration ($mmol/dm^3$) **Mycelium diameter (cm)**	CT_1 3.05	CT_2 1.54	CT_3 0.77	CT_4 0.38	CT_5 0.19	Control sample
I measurement	0	0	0	0.5	2	8.8
II measurement	0	0	0	0.3	1.7	8.8
III measurement	0	0	0	0.2	1.8	8.8
IV measurement	0	0	0	0.2	2.1	8.9
Average	0	0	0	0.3	1.9	8.8
Legend: CT −Cabrio top				**LSD (0.01) = 0.191**		

Table 2. Inhibition effect of newly synthesized $Cu[L-H]_2 (H_2O)_2$ complex against the fungal mycelium *Ph. viticola*

Concentration ($mmol/dm^3$) **Mycelium diameter (cm)**	C_1 1.78	C_2 0.89	C_3 0.44	C_4 0.22	C_5 0.11	Control sample
I measurement	6.2	7.1	7.5	8.6	8.6	8.8
II measurement	6.3	7.1	7.4	8.6	8.7	8.8
III measurement	6.2	6.9	7.4	8.6	8.7	8.8
IV measurement	6.2	7.0	7.4	8.7	8.6	8.9
Average	6.2	7.0	7.4	8.6	8.7	8.8
Legend: C - $Cu[L-H]_2 (H_2O)_2$				**LSD (0.01) = 0.151**		

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In a series of four repeated measurements of the mycelium *Ph. viticola*, all concentrations of Cabrio top (3.09 mmol/dm^3, 1.54 mmol/dm^3, 0.77 mmol/dm^3, 0.38 mmol/dm^3 and 0.19 mmol/dm^3) caused inhibition of the mycelium *Ph. viticola* in comparison to control sample. (Table 1) in accordance to the applied test LSD (0.01) = 0.151.

All applied concentrations of Cu[L-H]$_2$ (H_2O)$_2$ complex had a weaker inhibition of mycelia growth compared with conventional Cabrio top fungicide, however, all of the above mentioned concentrations ligand inhibited mycelia growth compared to the control. The deviations of the measured diameter of mycelium *Ph. viticola* are 2.6cm , 1.8cm , 1.4cm , 0.2cm and 0.1 cm (Figure 5).

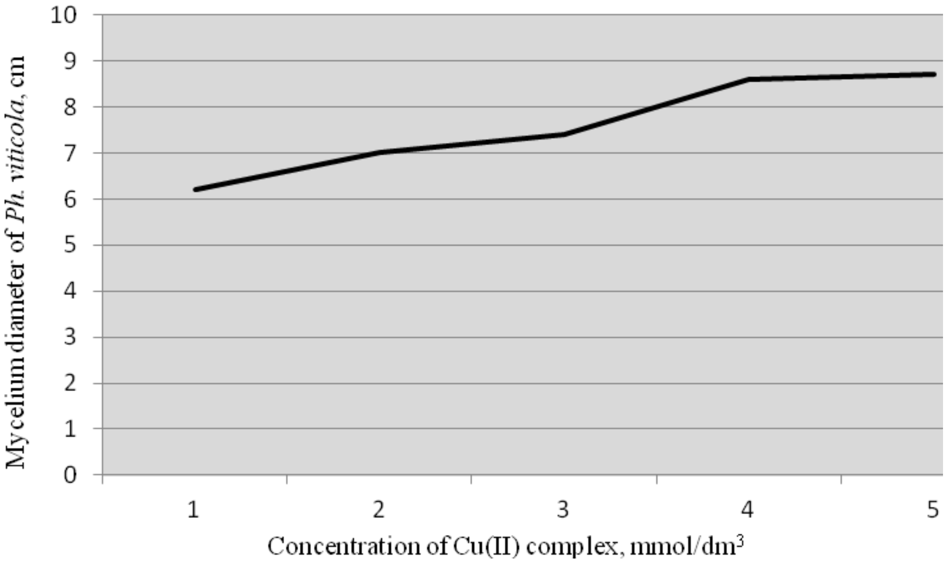


Figure 5. Graphic scheme of influence of the applied concentrations range (1.78- 0.11 mmol/dm^3) newly synthesized Cu[L-H]$_2$ (H_2O)$_2$ complex on mycelia *Ph. Viticola*

4. CONCLUSION

A Cu(II) complex via reaction of methanol solvent $Cu(CH_3COO)_2{\cdot}H_2O$ and methanol solvent pyrazole derivative L= 1,3-dimethyl-1H-pyrazole-5-carboxylic acid in mole ratio 1:2, with general formula Cu[L-H]$_2$(H_2O)$_2$ was produced.

Statistical results obtained from biological research (LSD(0.01) = 0.191 and LSD(0.01) = 0.151) show that all concentrations within the range (3.09– 0.19 mmol/dm^3) of the commercial fungicide Cabrio top and all concentrations within the range (1.78- 0.11 mmol/dm^3) of the newly synthesized Cu[L-H]$_2$(H_2O)$_2$ complex used have shown a significant inhibitory effect on Ph. viticola comparing to the control samples. These results of biological research indicate on investigation and determination new active component of fungicide.

References

[1] Jaćimović Ž. , 1998, Synthesis and structure of the complexes of Zn (II), Cd (II), Hg (II) and Cu (II) with a di and trisubstituted pyrazole derivatives, (*Doctoral dissertation*) , Faculty of Sciences Novi Sad

[2] Radović A, 2010, Physico-chemical characterization of some pyrazole derivatives and some newly synthesized Ni complexes and their biological efficacy in the inhibition of mycelial *Phomopsis viticola Sacc. (Sacc.)*, (*Master thesis*), Faculty of Metallurgy and Technology, University of Montenegro

[3] Chinese Journal of pesticides, Progresses on the Pyrazole Derivatives as Agrochemical Fungicides, 2005. Vol.44 No11, page 491-495,

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
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ISBN: 978-960-6865-94-7

[4] A list of active substances authorized for use in plant protection products (*Sl list Crne Gore 07/2014.)*
[5] Australian Pesticides and Veterinary Medicines Authority, 2003., Evaluation of new active pyraclotrobin in the product Cabri fungicide Canberra, Australia
[6] Jaćimović Ž, Kosović M., Novaković S., Giester G., Radović A., Synthesis and crystal structure of Cu(II) and Co(II) complexes with 1,3-Dimethyl-pyrazole-5-carboxylic acid ligand, *Journal of the Serbian Chemical Society*, 2015, 80, 1-12, ISSN/ISBN 0352-5139, DOI: 10.2298/JSC140722009J
[7] Stanković, J., Lakić, N., Ljubanović-Ralević, I.: *Exercises in experimental statistics*, University of Belgrade, Faculty of Agriculture. P. 242. (1990) (in Serbian)

Global Environmental Changes

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Parasites in the field of water: public health implications, influences by climate changes and research needs

P. Karanis[1*], G. Karanis[1,2]

[1] Centre for Biomedicine and Infectious Diseases (CBID), Qinghai Academy for Animal and Veterinary Science of the Qinghai University, Xining, R. P. China.
[2] Qinghai University Affiliated Hospital Xining, Medical School of Qinghai University, Xining, R. P. China.
*Corresponding author: Email: panagiotis.karanis@uk-koeln.de

Abstract

The purpose of this presentation is to provide an overview of the occurrence, transmission and control of water-related and water-borne parasitic diseases. The different types of water-related and water-borne parasites, the dynamics of transmission in the nature, from vectors (water or mosquitoes) to humans, and the prevention and control of water-related and water-borne parasites in our environment are shown, also in possible association with climate change and its influences. For the diagnosis and control of infectious diseases, the development of new molecular technologies and their applications are addressed. The investigation of clinical and environmental materials will help to determine parasitic sources, the activities of vectors and hosts for faster response to control the transmission ways of pathogens. So, the medical community could be well prepared for outbreaks and unexpected and challenging environmental and climatic events.

Keywords: climatic changes; parasites; public health; water treatment

1. CLIMATE CHANGE

Climate change looks too big to ignore.
The famous NASA climate scientist James E. Hansen warns: "I was too optimistic, climate change is much quicker than I expected !" [1].

The change of climate - accepted fact of science:
Global climate is not constant but subject of constant change. Reasons for this change are a variety of driving mechanisms [2]. As climate is a dynamical system it is influenced by external forces and internal processes. The change of climate is an accepted fact of science and had affected the world’s system in all sectors and in all times [3].

Driving forces on climate changes:
Since genesis of earth natural phenomena like solar forcing, greenhouse effect, volcanic forcing, ocean current and the continental drift have globally formed and modified the world’s climate.

1.1. Anthropogenic driving forces on climate change: human's responsibility

According to the IPCC (Intergovernmental Panel on Climate Change), the global warming during the second half of the 20th century is not explainable to be originated by natural factors solely. Referred to the IPCC, human activity entailed since 1750 collectively to global warming “very probable” which is defined as 90-99% likelihood [4].

Greenhouse gases – that are carbon dioxide (CO_2), methane (CH_4), nitrogen oxide (N_2O), ammonia (NH_3), fluorocarbon (FC), ozone (as secondary product) -, deforestation, livestock breeding and agriculture are mainly involved on climate changes.

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1.1.1. Greenhouse gases

The scientist Arrhenius stated in 1896 that the global warming could be enforced by humans adding CO_2 to the atmosphere [5]. As carbon dioxide is one of the greenhouse gases the release of carbon in the atmosphere resulted in a rise of greenhouse gases concentrations and consequently in a rise of the greenhouse effect and following warming up the world's temperature. Between 1958 and 2008 the atmospheric CO_2 concentration raised from 316 ppmv to 387 ppmv while the CO_2 concentration during the last 650000 years fluctuated from 180 ppmv to 300 ppmv. Concluded, one century of human pollution is analogical to thousands of years of natural development [6]. Since 1750 the concentration of CO_2 in the atmosphere has raised more than 30%. Approximately, one third of this amount stays in the atmosphere and one third is incorporated by the ocean and the last third will gather in the environment. As CO_2 has an impact on the radiation balance of the atmosphere it can enhance the global warming by trapping the heat reflected to the earth's surface [3]. The physics of surface warming as a result of atmospheric greenhouse gases is understood but rapidity and level of the rising is unknown and several climate models varies in their prediction [7, 8].

1.1.2. Deforestation

Another anthropogenic factor which enhances climate change is the deforestation. According to the United Nations Framework Convention on Climate Change (UNFCCC) office, the overwhelming direct cause of deforestation is agriculture. Subsistence farming is responsible for 48% of deforestation; commercial agriculture is responsible for 32% of deforestation; logging is responsible for 14% of deforestation and fuel wood removals make up 5% of deforestation [9].

The alteration of forests into agricultural land leads in two ways to a global warming: at first, slash-and-burn-agriculture releases greenhouse gases. On the other hand, forests – especially tropic forests such as in Brazil and Indonesia - serve as carbon dioxide storage and can release great amounts of carbon back to the atmosphere when destroyed – then exacerbate the greenhouse effect and global warming [10, 11]. Additionally, at higher temperatures the forests' ability of carbon clearing becomes less efficient [12]. So forests can be either sinks or sources for carbon depending upon environmental circumstances.

One fifth of all greenhouse gases results from the destruction of forests and change of land use. Studies of an international team of experts from the US, UK, Brazil and France to compare data from 11 climate-carbon computer models [12] confirm that deforestation in the tropics accounts for about 20 per cent of carbon emissions due to human activities. It was found out that if by 2050 deforestation was slowed down by 50 per cent from current levels, with the aim of stopping deforestation when 50 per cent of the world's tropical forests are remaining, this would save the emission of 50 billion tons of carbon into the atmosphere. This 50/50/50 option would avoid the release of the equivalent of six years of global fossil fuel emissions [12].

The removal of trees without sufficient reforestation also results in damage to habitat of any creature and plant and biodiversity loss. Deforestation reduces the content of water in the soil and groundwater as well as atmospheric moisture and results in aridity and desertification.

China's floods in the year 1999 after the great Yangtze and Yellow river had broken their banks, the discussion started weather the big deforestation in China could be one reason [13]. On the one hand flooding is the consequence of the natural cycle of seasonal change, but on the other hand deforestation is responsible for lower reaches of rivers and soil erosion. Sediment is washed downstream from mountainous areas and arrives in the central and lower regions of the rivers where this sediment raises the riverbed, so that the level of the water raises much higher than normal. Instead absorbing precipitation and leading it into the groundwater deforested soil become sources of surface water runoff, which moves much faster than subsurface flows and may lead into floods.

Concurrent there is a significant loss of important flood plain waterways. In China by the flood event year 1999 around 60% of the wetlands had been transformed into farmland in the lower and central regions of the Yangtze river [13].

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Trees in general influence the water cycle significantly: control of humidity of the atmosphere by transpiring, influence on occurrence of precipitation influence on capacity of soil to store water, producer of fresh water. As a result, the presence or absence of trees can change the quantity of water on the surface, in the soil or groundwater, or in the atmosphere. This changes the availability of water for either ecosystem functions or human services.

Peter Walker, director of disaster policy at the International Federation of Red Cross and Red Crescent Societies, said to the BBC news in August 1999 "You cannot grow a forest overnight, it will take years" [13].

There is the unconditional need to preserve the forests and reduce deforestation for stabilizing atmospheric greenhouse gas concentrations and to stabilize soil to prevent land loss and floods and loss of biodiversity.

2. CURRENT SITUATION OF IMPORTANT FOOD-, WATER- AND VECTOR-BORNE INFECTIOUS DISEASES

Infectious diseases are determined by pathogens, hosts and the environment (Table 1). Climate influences all these factors and thus plays an important role in the prevalence of infectious diseases [14, 15]. While climate is an important factor for health as it has an influence on the repertoire of infectious diseases weather can even affect the intensity of disease outbreaks [16]. A warming and instable climate will influence the global emergence and re-emergence of infectious diseases [17]. Between 1975 and 1995, more than 30 new infectious diseases like AIDS, Ebola and Lyme disease occurred [18]. Referred to the World Health Organization (WHO), infectious diseases which have a climate sensitivity and should be avoided by an early warning system (EWS) are: cholera, malaria, meningococcal meningitis, Dengue/ Dengue hemorrhagic fever, African trypanosomiasis, Yellow fever, Japanese encephalitis and St. Louis encephalitis, Rift Valley fever, Leishmaniasis, West Nile virus diseases, Ross River fever, Murray Valley encephalitis and Influenza [19]. The water-borne parasite *Cryptosporidium* has recently been recognized as one of the main reason for severe diarrheal disease [20]. Transmission is supported via water and food. Cryptosporidiosis is increasingly identified as an important cause of morbidity and mortality. In sub-Saharan Africa and south Asia *Cryptosporidium* was one of the most common identified pathogens of severe diarrheal disease during the first two years of life. 800,000 children under five die worldwide because of cryptosporidiosis diarrhea every year [20].

2.1. The impact of climate changes on pathogens

2.1.1. Effects of climate changes on infectious diseases in general

Climate changes and variables could drive vector-borne transmission and the seasonal dynamics of mosquito populations. For these reasons it is necessary to identify climate variables that are most affecting seasonal dynamics of for example floodwater which allow the distribution of mosquitos along the rivers.

Clinicians should be aware that the diseases are not confined to long-established endemic areas [21]. Diseases can spread to areas that have been considered non-endemic previously - caused by climate changes [22]. This was the case for example for leishmaniasis. As temperature can significantly affect the distribution of vectors, it also affects the metabolism of the vectors – as found in sandflies - and their developmental times. Consequently the vector's metabolism can affect the life cycle of the pathogen inside the vector [21].

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Table 1 Examples for pathogens linked to food-, water- and vector-transmission

Pathogen	Disease	Transmission	Clinical features
Protozoa			
Giardia duodenalis [syn.*G. lamblia, G. intestinalis*]	Giardiasis	Fecal-oral spread through drinking water or recreational water, soil, food, animal contact	Diarrhea, abdominal pain, weight loss, failure to thrive gas, abdominal cramps, upset stomach, nausea, dehydration
Cryptosporidium spp.	Cryptosporidiosis	Fecal-oral spread through drinking water or recreational water, soil, food, animal contact	Diarrhea often prolonged, stomach cramps or pain, dehydration, nausea, vomiting, fever, weight loss
Cyclospora cayetanensis	Cyclosporiasis	Fecal-oral spread through drinking water, soil, food	Diarrhea, abdominal pain, weight loss, failure to thrive
Entamoeba histolytica	Amoebiasis	Fecal-oral spread through drinking water, soil, food	(Bloody) diarrhea, maybe severe dysentery, weight loss, fatigue, abdominal pain, amoebic liver abscess
Toxoplasma gondii	Toxoplasmosis	Fecal-oral spread through drinking water contaminated by feline animals, row and under-cooked meat, soil, raw vegeta-bles, fruits, blood transfusion, organ transplant, transplacental transmission to fetus	Asymptomatic in healthy humans; flu-like symptoms, esp. in immune suppressed humans severe symptoms, neurological disorders, glandular fever, fetal damage in pregnant women, schizophrenia
Trypanosoma spp.	Trypanosomiasis Chagas Disease	Tsetse fly bite Triatoms	Fever, swollen lymph glands, muscles and joint pain, headaches, neurologic. symptoms: changes in personality, alteration of the biological clock (the circadian rhythm), confusion, slurred speech, seizures, difficulty in walking and talking, irritability
Free-living amoebae [FLA]	Granulomatous amoebic meningoencephalitis (GAE)	Aspiration of infected surface water into nose, heating/ ventilating /air conditioning systems, contact with contaminated soil, water, sewage, swimming pools, contact lens equipment	Fatal encephalitis – esp. in individuals with weak immunological conditions, acanthamoeba keratitis and corneal ulcers, granulomatous skin lesions
Plasmodium spp.	Malaria	Mosquito bite	Periodic fever and shivering, hemolytic anemia, flu-like symptoms, headache, joint pain, gastro- enteritis and vomiting, septicemia, retinal demage, neurological symptoms including nystagmus, conjugate gaze palsy, seizures, opisthotonus, convulsions, several serious complications
Leishmania spp.	Leishmaniases 1. Cutaneous form 2. Mucocutaneous 3. Visceral form (“Kala Azar”)	Sandfly bite	1. Widespread skin lesions which resemble leprosy, may not heal on its own 2. Skin and mucosal ulcers of nose and mouth 3. Fever, anemia, splenomegalia, fatal if untreated

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Table 1 (continued)

Pathogen	Disease	Transmission	Clinical features
Babesia spp.	Babesiosis (Human babesiosis is uncommon, but reported cases have risen recently)	Tick bite	Mostly asymptomatic, mild fever, diarrhea
		Helminths	
Schistosoma spp.	Schistosomiasis ("Bilharzia")	Contact with surface water infected with free swimming cercariae	Anemia, malnutrition, eosinophilia, fever, hepatosplenomegaly, portal hypertension, esophageal varices, pulmonary hyper- tension, cerebral granulomatous disease, glomerulo- nephritis, urinary and intestinal damage, bladder cancer
Dracunculus medinensis	Dracunculiasis (= guinea worm disease (GWD))	Drinking water contaminated with copepods (water fleas) infested with guinea worm larvae	Painful ulcers on lower limbs and feet
Bacteria			
Vibrio cholera	Cholera	Drinking water or eating food contaminated by infected feces	Watery diarrhea, vomiting, may be severe and fatal
Salmonella spp.	Salmonellosis	Occasional outbreaks with drinking water	Bloody diarrhea with mucus, colicky abdominal pain, fever, reactive arthritis (Reiters syndrome) possible
Salmonella typhi	Typhoid	Drinking water contaminated with infected feces	Fever, bradycardia (Faget sign), malaise, diarrhea, abdominal pain, epistaxis, hepatosplenomegaly, may be fatal
Shigella spp.	Shigellosis (bacillary dysentery)	Drinking water and recreational water	Diarrhea frequently with blood loss
Campylobacter spp.	Campylobacteriosis	Drinking water and recreational water	Diarrhea frequently with blood loss
Enterotoxigenic *E. coli* (ETEC)	"Travelers' diarrhea"	Drinking water	Watery diarrhea, enterohemorrhage
E. coli	Varies	Fecally contaminated drinking water and recreational water	Gastroenteritis, bloody diarrhea, urinary tract infections, hemolytic- uremic syndrome in children, septicemia, pneumonia
Yersinia spp.	Yersiniosis	Drinking water	Fever, diarrhea, abdominal pain
Francisella tularensis	Tularaemia	Drinking water	Typhoid-like or mucocutaneous and suppurative skin lesions
Helicobacter pylori	Gastritis	Possible routes of infection: oral-oral, fecal-oral, iatrogenic, drinking water, flies	Gastritis, dyspepsia, gastric ulcers, can progress to gastric cancer
Mycobacteria spp.	Varies	Potable water systems in hospitals, some recreation	Varies: respiratory disease, wound infections, skin disease
		Viruses	
Hepatitis A (HAV) and *Hepatitis E virus* (HEV)	Viral hepatitis	Eating or drinking food or water contaminated with infected feces, recreational water contact	Hepatitis with nausea, vomiting, diarrhea, yellow skin (jaundice), fever, abdominal pain
Norovirus, esp. Norwalk-like viruses	Viral gastroenteritis	Fecally contaminate food or water, person-to-person contact, aerosolization of the virus, contact with contaminated surfaces	Nausea, forceful vomiting, watery diarrhea, abdominal pain

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Table 1 (continued)

Pathogen	Disease	Transmission	Clinical features
Enterovirus spp. including poliovirus and Coxsackie virus	Various, including poliomyelitis and hand, foot and mouth disease	Drinking and recreational water contact, fecal-oral transmission	Variety of symptoms: mild respiratory illness (common cold), hand, foot and mouth disease, hemorrhagic conjunctivitis, aseptic meningitis, myocarditis, severe neonatal sepsis-like disease, acute flaccid paralysis
Rabies Virus	Rabies	Bite or scratch by an infected animal	Beginning with flu-like symptoms, rapidly developing paralysis, anxiety, insomnia, confusion, agitation, abnormal behavior, paranoia, terror, hallucinations, delirium, death (survival rate 8%)
Influenza A Virus spp.	Avian influenza (= bird flu)	Contact with dead infected birds or infected fluids	Flu-like symptoms, may develop fatal
Dengue Virus	Dengue Fever	Mosquito bite	Fever, headache, muscle and joint pains, characteristic skin rash similar to measles, may develop into life- threatening dengue hemorrhagic fever with bleeding, low levels of blood platelets, blood- plasma leakage, or into dengue shock syndrome
Yellow Fever Virus	Yellow Fever	Mosquito bite	Fever, headache, chills, back pain, loss of appetite, nausea, vomiting, toxic phase: jaundice due to liver damage, abdominal pain. Bleeding in mouth, eyes, gastro- intestinal tract causing bloody vomiting ("black vomit")
West Nile Virus	• West Nile fever (WNF) • West Nile neuroinvasive disease (WNND) • West Nile virus encephalitis (WNE) • West Nile meningitis (WNM) • WestNile meningoencephalitis • West Nile poliomyelitis (WNP)	Mosquito bite	Additionally various nonneurologic complications (hepatitis, pancreatitis, myocarditis, rhabdomyolysis, orchitis, nephritis, optic neuritis, cardiac dysrhythmias, hemorrhagic fever with coagulopathy and cutaneous manifestations possible
Japanese encephalitis virus	Japanese encephalitis	Mosquito bite	Fever, headache, 1 in 250 infections develop into encephalitis with neck rigidity, cachexia, hemiparesis, convulsions

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Table 1 (continued)

Pathogen	Disease	Transmission	Clinical features
Saint Louis encephalitis virus	Saint Louis encephalitis	Mosquito bite	Fever, headache, encephalitis similar to Japanese encephalitis symptoms
Ross River Virus	Ross River Fever	Mosquito bite	Influenza-like-illness, polyarthritis, arthalgia, rash
Murray Valley Encephalitis Virus (MVEV)	Murray Valley encephalitis (MVE)	Mosquito bite	Fever, headache, nausea, vomiting, in rare cases MVE with permanent neurological disease or death
SARS coronavirus (SARS-CoV)	Severe acute respiratory syndrome (SARS)	Contact to contaminated bats and palm civets, person-to-person	Nonspecific flu-like symptoms
Algae			
Cyanobacteria	Various	Toxins in drinking water or direct contact with surface water blooms	Neuro-, hepato-, cyto-, endotoxins may cause diff. diseases, dermatitis, hepatitis, respiratory symptoms, involved in amyotrophic lateral sclerosis ALS, potentially fatal
Pfiesteria piscicida	Estuary-associated syndrome	Toxins in water	Respiratory, gastro- intestinal and eye irritation, acute skin burning (on direct contact with water), muscle cramps, headache, deficiency in learning and memory, confusion
Fungi			
Aspergillus	Aspergillosis: chronic pulmonary aspergillosis (CPA), aspergilloma, allergic bronchopulmonary aspergillosis (ABPA)	Inhalation, entering bloodstream via lungs	Chronic, invasive or allergic forms, Pneumonia, fever, chest pain, dyspnea, cough, blood clots, risk of dissemination throughout the body infecting major organs in case of deficient immune system, kidney and liver failure, otomycosis, fungal sinusitis, keratitis, onychomycosis
Candida	Candidiasis	Candida are generally present in healthy humans, but overgrow normal flora in case of weakened or undeveloped local or systemic immune response or metabolic illnesses	Superficial, local or systemic and potentially life-threatening symptoms (skin, nails, genitalia, respiratory and gastrointestinal tract), fungemia called candidemia in immunocompromised humans
Cryptococcus	Cryptococcosis	Inhalation from the environment	Rarely occur in immunocompetent humans, fever, fatigue, chest pain, dry cough, swelling of abdomen, headache, blurred vision and confusion, meningitis

Runoff fluxes and pathogen release will be affected, either positively or negatively, however, the real effects on the pathogen concentration in surface waters and their transmission via water and food remains unknown. *Cryptosporidium* and *Giardia* are parasitic protozoa that constitute the leading causes of waterborne enteric disease outbreaks worldwide but many other pathogens are causes of enteric diseases transmitted via drinking water or eating food contaminated by infected feces (see table 1). Understanding the distribution of waterborne protozoa species in environmental

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waters and keep in mind that the climate changes will have an influence in their distribution and transmission is a good basis to improve the existing regulatory monitoring and water quality management.

3. WHAT IS POSSIBLE TO DO FROM THE SITE OF THE MEDICAL COMMUNITY TO PREVENT THE DISTRIBUTION OF INFECTIOUS DISEASES

This is a call for attention to the developments of new and useful molecular technologies and specifically its application for the control of infectious diseases in association with climatic changes.

It is important to identify not only the occurrence and prevalence but also the level of burden and at best the source of contamination with any pathogen (water-, food-, and vector-borne) to maximize the public health surveillance. During the drinking water purification, particularly the monitoring of common protozoa like *Giardia* and *Cryptosporidium* is requested by reason that they belong to the most frequently detected causes of waterborne parasitic protozoan disease outbreaks. Care should be given as their infectious dose is low. Detection and identification methods of waterborne parasitic protozoa should be standardized and easily accessable for everybody worldwide and should be component of clinical routine screening investigations [23].

3.1. Loop-mediated isothermal amplification (LAMP) – as an example for a new and useful molecular technology for monitoring and investigations of environmental influencing substrates helping to protect and heal/restore

The LAMP was developed as nucleic amplification test (NAT) and was declared to have “high specificity, efficiency and rapidity” [24]. Ever since, the LAMP outmatches the PCR as molecular method because it is more effective and less sensitive to contamination of the target DNA [25]. For this method, only a robust polymerase (BST) and four primers recognizing six different sequences of the targeted DNA are required [26]. After 1 hour in a constant temperature of 60-70°C DNA, fragments of different lengths which can be easily detected are existent. Due to the design of this method, a high specificity towards the DNA sequences is gained [25]. Karanis and Ongerth (2009) provided an overview and they described the high potential for extensive applicability of the LAMP [26].

3.1.1 Application possibilities of LAMP detection method

Since its development in the beginning of the year 2000, LAMP has been widely applied for detection and analysis of nucleic acid sequences, especially those derived from pathogenic microorganism. Over the years, a vast number of protocols have been published that are more or less applicable for detection of a variety of pathogens including viruses, bacteria, fungi and worms, amongst other. The development was fostered by establishment of appropriate RT-LAMP assays, which can amplify RNA with the addition of reverse transcriptase, in analogy to RT-PCR [27]. The scope of use of LAMP has been extended to more sophisticated applications like sex identification of animal embryos and living animals, tumor detection and detection of food ingredients with genetically modified contents. In practical terms, LAMP assays suitable for in-field-analysis and for application in rural hospitals and resource-limited hospital laboratories have become more and more important.

In virus detection, LAMP has come to popularity after 2003 following SARS and West Nile virus emergence. Naturally, the vast majority of papers deal with the detection and differentiation of more prominent virus classes, i.e. *Herpesviridae, Hepadnaviridae,* and *Retroviridae*. LAMP assays are capable of diagnosing viral infections in many sub-domains of human medicine. Besides hepatitis, HIV and viral hemorrhagic fever, multiple pathogens for viral gastroenteritis, respiratory

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infections and childhood diseases can be detected by LAMP with a high sensitivity and specificity. In the context of veterinary medicine, LAMP was successfully applied for diagnosing rabies, avian influenza, foot-mouth disease and multiple viral diseases in fish and shrimp. Furthermore, detection of several plant pathogenic viruses has successfully been demonstrated by LAMP.

3.2. Future perspective

From the perspective of the medical community, for preventing the distribution of infectious diseases, the accurate diagnosis of pathogens and diseases at any time and particular during outbreak events and epidemics is the premise; it is necessary to provide alternative possibilities and make it possible to respond rapidly to risky situations in order to protect the public health. Future research must be shifted to the conclusions of basic research efforts that also include findings on the developmental stages and life cycles of the pathogens. In addition to the above mentioned topics the reader is requested: Hold the future directions and challenges in front of eyes - the challenges that still lie ahead of us.

Literature

[1] Hansen J., Sato M., Ruedy R.,., 2012. Perception of climate change. *National Aeronautics and Space Administration Goddard Institute for Space Studies and Columbia University Earth Institute, New York, NY 10025; PNAS,* **109 (37)**, E 2415-2423.

[2] Schwarz R., Harmeling S., Kie, G., Bals C. (2008). *Globaler Klimawandel: Ursachen, Folgen, Handlungsmöglichkeiten.* 2nd ed., Germanwatch, Bonn, Germany.

[3] Stocker T., 1999. Abrupt climate changes: from the past to the future – a review. *Int Journal Earth Sciences*, **88**, 365-374.

[4] http://ipcc.ch/report/ar4/wg1/. Climate change 2007: The physical science basis. (accessed March 15th, 2014).

[5] Weart S.R., 2003. *The discovery of global warming.* 1st ed., Harvard University Press, Cambridge, UK.

[6] Maslin M., 2005. *Global warming, a very short introduction.* 1st ed., Oxford University Press, USA.

[7] Costello A., Abbas M., Allen A., Ball S., Bell S., Bellamy R., Friel S., Groce N., Johnson A., Kett M., Lee M., Levy C., Maslin M., McCoy D., McGuire B., Montgomery H., Napier D., Pagel C., Patel J., Antonio J., de Oliveira P., Redclift N., Rees H., Rogger D., Scott J., Stephenson J., Twigg J., Wolff J., Patterson C., 2009. Managing the health effects of climate change. *Lancet* **, 373**, 1693–1733.

[8] Keller C., 2003. Global warming: The balance of evidence and its policy implications. *Scientific World Journal***, 3**, 357-411.

[9] http://unfccc.int/files/essential_background/background_publications_htmlpdf/application/pdf /pub_07_financial_flows.pdf. Investment and financial flows to address climate change. P. 81. (accessed March 15th, 2014).

[10] http://www.tigweb.org/express/panorama/article.html?ContentID=7611. Mumoki F., 2006. The effects of deforestation on our environment today. (accessed Februar 10th, 2014).

[11] nhttp://www.wwf.de. (accessed March 18th, 2014).

[12] Gullison R.E., Frumhoff P.C., Canadell J.G., Field C.B., Nepstad D.C., Hayhoe K., Avissar R., Curran L.M., Friedlingstein P., Jones C.D., Nobre C., 2007. Tropical forests and climate policy. *Science*, **(316) 5827**, 985-986.

[13] http://news.bbc.co.uk/2/hi/asia-pacific/413717.stm. World: Asia-Pacific China's floods: Is deforestation to blame? (accessed April 18th, 2016)

[14] Karanis P., Kourenti C., Smith H., 2007. Waterborne transmission of protozoan parasites: a worldwide review of outbreaks and lessons learnt. *Journal of Water and Health*, **5**, 1-38.

[15] Epstein P., 2001. Climate change and emerging infectious diseases. *Microbes Infection***, 3**, 747-754.

[16] Dobson A., Carper R., 1993. Biodiversity. *Lancet*, **342**, 1096–1099.

[17] McMichael A.J., Haines A., Slooff R., Kovats S., 1996. Climate change and human health. *Climatic Change* **38 (4)**, 501–506, .

[18] http://www.who.int/whr/1996/en/. The world health report 1996. Fighting disease, fostering development. (accessed February 10th, 2014)

[19] Kuhn K., Campbell-Lendrum D., Haines A., Cox J., 2005. *Using climate to predict infectious disease epidemics.* World Health Organization, Geneva, Switzerland.

[20] Checkley W., White A.C. Jr., Jaganath D., Arrowood M.J., Chalmers R.M., Chen X.M., Fayer R., Griffiths J.K., Guerrant R.L., Hedstrom L., Huston C.D., Kotloff K.L., Kang G., Mead J.R., Miller M., Petri W.A. Jr, Priest J.W., Roos D.S., Striepen B., Thompson R.C., Ward H.D., Van Voorhis W.A., Xiao L., Zhu G., Houpt E.R., 2015. A review of the global burden, novel diagnostics, therapeutics, and vaccine targets for *Cryptosporidium*. *Lancet Infect Dis.,* **15(1)**, 85-94.

ISBN: 978-960-6865-94-7

[21] Hlavacova J., Votypka J., Volf P., 2013. The effect of temperature on *Leishmania* (Kinetoplastida: Trypanosomatidae) development in sand flies. *Journal Medical Entomology***, 50**, 955-998.
[22] Stafford K.,C., Williams S.,C., Magnarelli L. A, Bharadawj A., Ertel S.H., Nelson R.S., 2014. Expansion of zoonotic babesiosis and reported human cases, Connecticut, 2001-2010. *Journal Medical Entomology*, **51**, 245-252.
[23] Skotarczak B., 2009. Methods for parasitic protozoans detection in the environmental samples. *Parasite***, 16**, 183-190.
[24] Notomi T., Okayama H., Masubuchi H., Yonekawa T., Watanabe K., Amino N., Hase T., 2000. Loop-mediated isothermal amplification of DNA. *Nucleic Acids Research*,15, **28 (12)**, E63.
[25] Skotarczak B., 2010. Progress in the molecular methods in the detection and genetic characterization of *Cryptosporidium* in water samples. *Ann Agric Environ Med***, 17**, 1-8.
[26] Karanis P., Ongerth J., 2009. LAMP-a powerful and flexible tool for monitoring microbial pathogens. *Trends Parasitology*, **25**, 498-499.
[27] Parida M., Posadas G., Inoue S., Hasebe F., Morita K., 2004. Real-time reverse transcription loop-mediated isothermal amplification for rapid detection of West Nile virus. *Journal Clinical Microbiology***, 42**, 257-263.

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Enabling new values chains for CO_2 reuse

A. Angelis-Dimakis*, A. Castillo-Castillo

Centre for Environmental Policy, Imperial College London, No. 14 Prince's Gardens,
London SW7 1NA, UK.
*Corresponding author: Email: a.angelis-dimakis@imperial.ac.uk

Abstract

A typical carbon reuse value chain consists of a CO_2 emitting industry (source), the carbon capture, treatment and purification facilities, the carbon transportation infrastructure and a CO_2 end receiving process (sink). All four steps are interrelated and the qualitative and quantitative characteristics/requirements of each one strongly affect the composition of the entire system. Thus, the design of a successful and technically feasible value chain and the subsequent formulation and implementation of an economically viable business model requires a holistic and systemic approach and a detailed analysis of all its components. This paper will attempt to address this issue by critically reviewing the major existing studies performed for all the stages and to formulate an overall methodological framework, towards enabling the creation of new value chains based on carbon dioxide reuse. An appropriate taxonomy of all the sources has been proposed, the physical requirements, the economic performance and the applicability of the major capture, treatment and purification technologies have been examined and potential clustering opportunities based on the quantity and quality requirements of the CO_2 conversion process have been identified.

Keywords: carbon capture utilization (CCU); systemic approach

1. INTRODUCTION

A generic CO_2 value chain is presented in Figure 1
Figure. However, the boundaries among the different stages or even their order in the chain are not very strict. For example, purification and treatment technologies are often considered to be the final stage of the capture process. The selection of the components in such a value chain depends on several factors. The choice of capture technology is mainly based on the CO_2 source and its main characteristics (mass flow, CO_2 purity, impurities and prevailing conditions - temperature and pressure of the process). On the contrary, the selection of purification and treatment technologies may vary depending on the chosen transport method and the CO_2 sink (terminal storage point or end use) and its quality requirements.

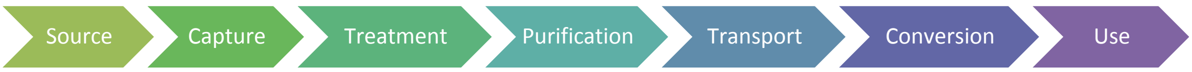


Figure 1. Generic carbon dioxide value chain

Thus, in order to propose, design and implement a technically feasible and economically viable value chain a systemic approach is necessary and detailed knowledge of all of its components is required. The current paper will present all the necessary information required to develop such a value chain. Sections 2-5 will address each one of its four main stages (source, treatment, transport and end-use) whereas Section 6 will examine the key parameters that affect its economic viability. Finally, Section 7 will summarize the key findings and suggests areas for further research.

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2. CARBON SOURCES

Currently, there are no unified or authoritative criteria for the classification of CO_2 streams and all existing classifications of the CO_2 concentration differ significantly between organizations and industries. In general, it can be stated that capturing and producing CO_2 as a "commercial" product generally depends on the availability of a relatively high-volume, CO_2-rich gas stream. However, from a business perspective, the most important factors related to the CO_2 source, which should be taken into account for a potential CO_2 reuse investment, are the cost of separating and purifying the CO_2 from the effluent gas stream and the energy required, if any. The effluent gas stream characteristics that strongly influence these two parameters are the concentration of CO_2 and the presence of impurities. Furthermore, another important factor that affects the economic viability of an investment is the available effluent gas flow per annum.

Concerning the effluent gas flow, the literature review has revealed that there are some non-statutory boundaries for classifying CO_2 sources, according to their size. IPPC states that CO_2 stationary sources should be considered "large scale" if they are emitting over 0.1 $MtCO_2$ per year (Mtpa) [1]. This threshold was selected because the sources emitting less than 0.1 Mtpa together account for less than 1% of the emissions from all the stationary sources. Several interviews with industrial stakeholders from the Port of Antwerp and the Stenungsund Industrial Park have guided towards specifying the boundaries for the other scales. The lower limit was decided following a statement from one of the interviewees that the minimum flow of CO_2 in order to even consider building a small pipeline, is 35ktpa. Thus, the proposed classification scheme for CO_2 sources is the following:

- Micro Scale: 0.035-0.075 Mtpa
- Small Scale: 0.075-0.1 Mtpa
- Moderate Scale: 0.1-0.5 Mtpa
- Large Scale: ≥0.5 Mtpa

For the stream classification based on CO_2 purity, some indicative specifications have been formulated by research projects or organizations, although there are no nationally or internationally agreed standards. The emphasis is mainly on pointing out the high-purity CO2 sources, which can be defined as the gas streams from which CO2 does not need to be separated, but that can be applied directly for CO2 utilisation and/or storage, only requiring compression and removal of water and minor impurities. According to a report by Carbon Counts [2], all CO_2 flue gas streams with CO_2 concentration greater than 80% can be classified as high purity, whereas Element Energy [3] listed natural gas processing, hydrogen, ammonia and biofuel production from fermentation as the most common sources of high purity CO_2, with average concentration in flue gas over 95%. Jin et al. [4] have classified CO_2 sources in four bins based on the impact of the CO_2 concentration on the energy requirements (and the resultant cost) for separating CO_2 from the gas stream. After consulting with the industrial stakeholders, it was decided that the most appropriate and simple classification scheme was the following:

- High Level: >90%
- Moderate Level: 20-90%
- Low Level: <20%

The third criterion, the presence of impurities, poses more difficulties in the classification due to (a) the large number of possible substances which may be considered impurities and (b) the fact that their presence in the gas stream depends on various parameters (i.e. fuel and raw materials used, conditions of the process etc.) which may differ between plants of the same product, even in the same industrial cluster. For these reasons this criterion was, initially, excluded from the classification matrix, which is presented in Table 1. The matrix is populated based on average literature values both for size and CO_2 concentration level and the values included are only indicative because (a) the size of the source heavily depends on the capacity of the industrial plant

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and (b) the purity level and CO_2 concentration in the effluent gas stream, especially for combustion related processes, depend on the quality/composition of the fuel used, the oxygen to fuel ratio during combustion and the detailed production process of each plant.

Table 1. CO_2 Sources Classification Matrix

	High Level (>90%)	**Moderate Level (20%-90%)**	**Low Level (<20%)**
Small Scale (<0.1 Mtpa)	Fermentation	-	-
Medium Scale (0.1-0.5Mtpa)	Ethylene Oxide Plant Syngas Production Ethanol Plant Methanol Plant	-	Biomass power plant Fluid Catalytic Cracking Pulp & Paper Mill
Large Scale (≥0.5Mtpa)	Ammonia Synthesis Natural Gas Sweetening Hydrogen Production Oxy-firing Process	Cement Production Kiln Flue Gas Scrubbing Blast Furnace Oxygen Blast Furnace	Coal Power Plant Natural Gas Power Oil Power Plant Oil Refineries Iron-Steel Mills Ethylene Plant Kraft Mill

3. CARBON CAPTURE TECHNOLOGIES

The objective of this section is not a detailed literature review of all the potential capture technologies. For that purpose, there exist several scientific papers [5] and publicly available reports and reviews [6, 7] which also describe in detail all the chemical reactions and relevant characteristics of these technologies. Our objective is to present a compact review of the most widely used technologies and emphasize on the characteristics that will be interesting for the formulation of a new value chain based on carbon dioxide reuse.

Carbon capture technologies can been classified in three categories: (a) post-combustion capture, (b) pre-combustion capture, and (c) oxy fuel combustion. Post combustion systems capture CO_2 from the flue gas which are produced after burning fossil fuels or other carbon-containing fuels. According to the technique used, they can be further classified in three categories:

- Absorption by chemical solvents
- Adsorption by solid sorbents
- Membrane separation

Absorption by chemical solvents is the most widely used technology for post-combustion capture of CO_2. Among the available chemical solvents, monoethanolamine (MEA) is the most widely used, because of its high reactivity with acid gases (like CO_2), its fast reaction time and its ability to remove high percentages of CO_2, even at low CO_2 concentrations. However, it is also characterized by high corrosivity, high energy consumption for desorption and relatively low limit on the maximum CO_2 loading capacity [8, 9]. Ammonia and the so-called second generation of solvents (such as ionic liquids) are also examined as potential solvents but are still in early stages of

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research for CO_2 capture [10].

Solid sorbents adsorb CO_2 on their surfaces, which is released by altering the temperature or the pressure change, leading to the regeneration of the original sorbent. Such a technology seems promising and may offer lower energy consumption but is still in the phase of technology validation [7]. Membranes in post combustion capture, are mainly used to separate CO_2 from N_2 and O_2. Due to low CO_2 partial pressure, a huge surface is required, making membranes one of the least favourable options since it is not economically competitive with amine-based post-combustion CO_2 capture and is not expected to be widely used unless high selectivity can be achieved [10].

Pre-combustion capture refers to the isolation of CO_2, which is the by-product of an industrial process (such as ammonia production and coal gasification) where no combustion is involved. In the case of power plants, carbon cannot be capture as it is in the fuels and must be converted to a more suitable form, in order to remove it from fuel prior to combustion. The more technologically advanced pre-combustion capture systems include chemical and physical solvents, which are used widely in natural gas and synthesis gas production. Absorption by chemical solvents is used to remove CO_2 when its partial pressure is low and the physical and chemical characteristics of the process are similar to the post-combustion capture. Physical absorption is an expensive process and requires a significant amount of energy for CO_2 capture. It is more applicable when the gas stream has a high CO_2 partial pressure and/or a high total pressure [1]. Solid sorbents or membranes are processes at the earliest stages of development and are not commercially available yet for pre-combustion capture [10].

In oxy-combustion processes, the fuel is burned with pure oxygen and not with air, thus avoiding impurities in the flue gas stream such as N (and its compounds NO and NO_2) or Ar, and the CO_2 capture efficiency reaches almost 100%. The disadvantage is the high cost of producing pure oxygen, due to the energy intensive air-separation process. Although oxy-fuel combustion technology is being steadily applied in the iron and steel (oxy fuel furnace) and glass melting industries today, the relevant CO_2 capture technologies have not yet been deployed on a commercial scale [1] and they are not expected to be commercially available before 2025-2030 [11].

4. CO_2 TRANSPORTATION

There are several options available for transporting CO_2 (e.g. onshore or offshore pipelines, tankers, railroad, trucks) and the selection is determined by:

- Quantity of CO_2;
- Distance and terrain morphology;
- Purity characteristics of the CO_2 stream; and
- Existing infrastructure

Usually, pipelines are the most cost effective means of transport for large quantities over medium distances, whereas ship transportation can be economically viable when the overall distance is relatively large (>1000 km) or over large bodies of water. Rail and road transport are rarely used and will be feasible for moving CO_2 on a small scale for specialised applications (Boot-Handford, et al, 2014). In any case, the CO_2 transport chain has one of the two following configurations:

- Source – Compression – Pipeline – Sink
- Source – Liquefaction – Storage – Loading – Truck/Ship – Unloading – Sink

5. CO_2 RECEIVING PROCESSES

CO_2 is currently used as an input in several industrial processes and the various technologies and products are currently in different stages of development. For the purposes of this analysis, a list of

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CO_2-receiving processes has been compiled based on an extensive literature review and the TRL of each one has been determined. TRL is a systematic metric system used to assess the maturity level of a technology, which varies from 1 to 9, with 9 being the most mature process. The most promising processes have been selected for the estimation of the potential for CO_2 utilization, based on their TRL, their inclusion in previous mapping attempts [12, 13] and the comments from the interviewed industrial stakeholders. For each one of the process, the most important design parameters and quality requirements have been collected [14, 15, 16, 17, 18, 19] and are presented in Table 2. Of course, the list is not exhaustive and one may argue that several important and widely applied or promising end-uses are missing (such as polymer production or algae production). However, the main objective of the list is to highlight the level of detail required for each end-use in order to formulate a CO_2 value chain and not present a complete inventory of CO2 receiving processes and their characteristics.

Table 2. Design parameters and quality requirements for CO_2 receiving processes

	TRL	**CO_2 to Product Ratio**	**Purity**	**P, T, Catalyst**	**Potential Synergies**
Horticulture Production	9	0.5–0.6 $kgCO_2/hr/100m^2$	Depends on crop), Avoid SOX, NOX & Heavy Metals	Low T, No Catalyst	Waste heat
Methanol Production	7-9	1 tCO_2 produces 0.728 t CH_3OH	Concentrated CO_2 source	High P (5MPa), High T (225^{o}C), Metal Catalyst	Water and excess energy supply, Low cost electricity
Urea Production	9	0.735–0.75 tCO_2 per t of urea	No quality requirements	High P, High T, No Catalyst	Ammonia production, natural gas sources
Carbon Mineralization	7-8	1 tCO_2 produces 1.916 t magnesite	No quality requirements, Avoid S	Optimal P: 40-150 atm, Optimal T: 100-180 °C	Industrial waste (slag, fly ash and waste water/brine)
Bauxite Residue Carbonation	9	30-50 $kgCO_2$ per t of red mud	High Purity (>85%)	High Pressure (4MPa)	Aluminium Industry
Concrete Curing	7-8	0.12 tCO_2 per t of precast concrete	No quality requirements	No Catalyst	Cement Industry

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6. DEVELOPING A CO_2 VALUE CHAIN

As it has been already mentioned, the development of new value chains requires a detailed knowledge of the technical characteristics of all involved stages. However, in order to formulate and implement sustainable business models, apart from the technical matching, the financial viability of the chain should be examined. As in any case where private companies are involved, one of their main objectives is to identify a profitable solution and to avoid reducing the net economic output of each stakeholder.

For a CO_2 source, this means that the cost of capture and treatment per tonne of CO_2 should be lower than the sum of the selling price of the captured stream, the carbon tax (paid by the company when emitting CO_2 to the atmosphere – ranging from 5-10€/tCO_2) and the profit margin. On the other hand, a potential CO_2 receiver needs to ensure that the cost of purchasing captured CO_2 and the investment required for any alterations required in the production process will be lower than the commercial price of the CO_2 plus the envisaged profit margin. To that end, it should be also taken into account that the company may potentially increase the price of their final product by advertising it as carbon neutral.

Critical parameters for the economic viability of a CO_2 value chain are obviously the agreed selling price of CO_2 (which eventually affects the economic output of both stakeholders) and the distance between the two facilities. The distance will also determine the means and subsequently the cost of transporting CO_2. An allocation of this figure to the involved stakeholders may be performed, only after taking into account the existing infrastructure in the region (e.g. unused pipelines, railway services). Thus, more detailed calculations about the viability of CO_2 value chains can be performed on a case by case basis, since the list of possible combination can be endless.

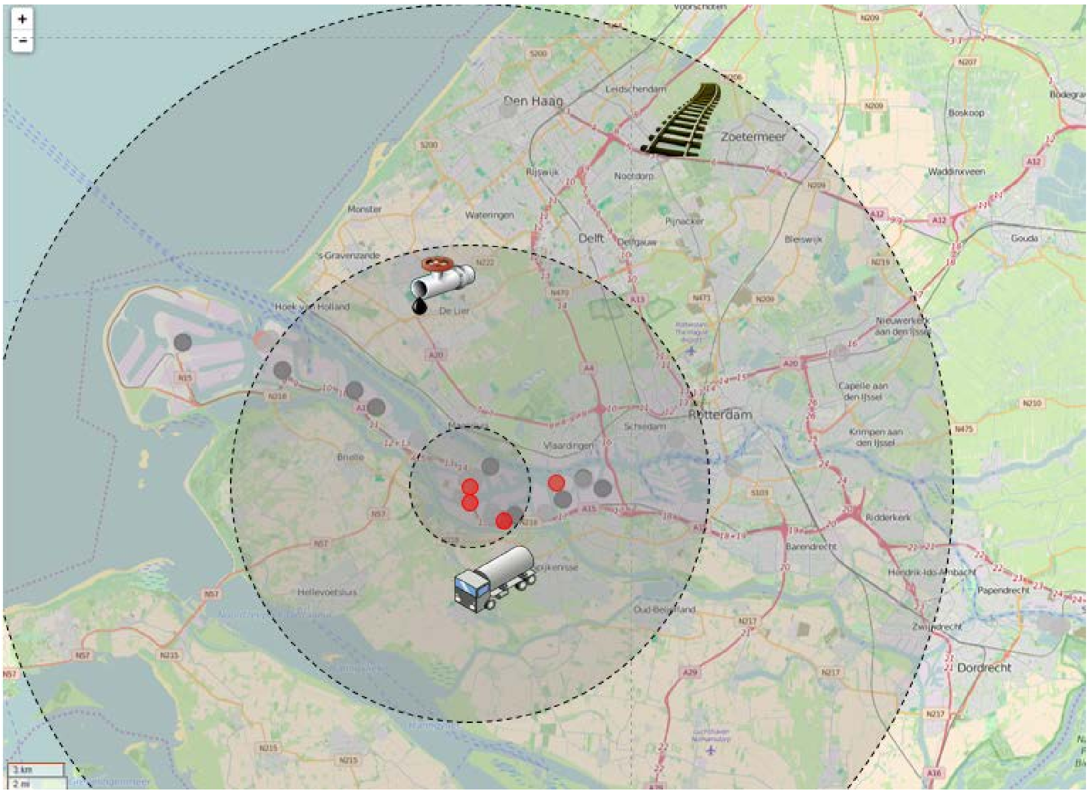


Figure 2. Profitable range of seeking sinks for a high purity source

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One way of extracting some generic conclusions is to approach the problem from the viewpoint of a carbon source, and determine the maximum distance that a CO_2 supplier can search for a potential buyer by having at the same time a positive net economic output. Figure 2 presents the results of the analysis for a medium scale - high purity source (where the only treatment required is compression), by assuming point-to-point transportation and its entire cost is being paid by the supplier. Data for the current level of carbon capture and transportation costs have been collected from the existing literature [3] and synthesized. The results show that the railway offers a bigger radius, with the limitation that railway is not connected to every point in the circle, and onshore pipelines is the next best solution. Trucks could only be considered for a small radius of 2-3 km around the facility.

7. CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

Formulating and developing a CO_2 reuse value chain is not a straightforward task because apart from the amount of flow, the purity and the physical and chemical properties of the stream should also be taken into account. Moreover, after identifying all technically acceptable solutions, the economic viability of all involved stakeholders should be examined. Detailed calculations can only be performed on a region specific example. More generic conclusions could be drawn by approaching the problem from the viewpoint of a carbon source, and determining the profitable range for seeking potential receiving processes.

Similar results could be achieved, by approaching the problem from the viewpoint of a carbon sink; either by determining the maximum distance where a potential supplier could be located (for existing businesses) or by identifying regions where all prerequisites for a receiving process are met and thus a new industrial facility could be built. Moreover, sensitivity and tipping point analysis need to be performed in order to account for the influence of scale and logistics costs in addition to capital costs of suitable capture and treatment technologies, and the anticipated rise in the carbon credit and the CO_2 commercial price in the future.

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References

[1] IPCC, 2005. *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[2] Carbon Counts, 2010. *High-purity CO_2 sources - Sectoral Assessment*. Final Draft Report. Contribution to UNIDO/IEA Technology Roadmap on CCS in industrial applications. Carbon Counts Company (UK) Ltd

[3] Element Energy, 2014. *Demonstrating CO_2 capture in the UK cement, chemicals, iron and steel and oil refining sectors by 2025: A Techno-economic Study*, Final Report for DECC and BIS, Element Energy Limited, Cambridge, UK.

[4] Jin, H., Gao, L., Li, S., van Sembeek, E., Porter, R., Mikunda, T., Dijkstra, J.W., de Coninck, H. and Jansen, D., 2012. *Supporting early Carbon Capture Utilisation and Storage development in non-power industrial sectors, Shaanxi Province, China*, Report No.12, The Centre for Low Carbon Futures.

[5] Boot-Handford, M.E., Abanades, J.C., Anthony, E.J., Blunt, M.J., Brandani, S., Mac Dowell, N., Fernandez, J.R., Ferrari, M.C., Gross, R., Hallett, J.P., Haszeldine, R.S., Heptonstall, P., Lyngfelt, A., Makuch, Z., Mangano, E., Porter, R.T.J., Pourkashanian, M., Rochelle, G.T., Shah, N., Yao J.G. and Fennell, P.S., 2014. Carbon capture and storage update. *Energy Environ. Sci.*, 7, 130-189.

[6] Styring, P., Jansen, D., De Coninck, H., Reith, H. and Armstrong, K., 2011. *Carbon capture and utilisation in the green economy: Using CO_2 to manufacture fuel, chemicals and materials*. The Centre for Low Carbon Futures 2011 and CO_2Chem Publishing 2012, ISBN: 978-0-9572588-1-5.

[7] GCCSI, 2011. *The global status of CCS*, Global CCS Institute, Canberra, Australia.
[8] Lee, J.Y., Keener, T.C. and Yang, Y.J., 2009. Potential flue gas impurities in carbon dioxide streams separated from coal-fired power plants. *J Air Waste Manag Assoc*. 59(6), 725-732.
[9] Rubin, E., Mantripragada, H., Marks, A., Versteeg, P. and Kitchin, J., 2012. The outlook for improved carbon capture technology, *Progress in Energy and Combustion Science*, 38(5) 630-671.
[10] Florin, N. and Fennell, P., 2010. *Review of Advanced Carbon Capture Technologies*. Work stream 2, Report 5A of the AVOID programme (AV/WS2/D1/R05A). Available online at www.avoid.uk.net
[11] Cuellar-Franca, R.M. and Azapagic, A., 2015. Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. *Journal of CO_2 Utilization*, 9, 82-102.
[12] Pérez-Fortes, M., Bocin-Dumitriu, A. and Tzimas. E., 2014. CO_2 Utilization Pathways: Techno-Economic Assessment and Market Opportunities, *Energy Procedia*, 63, 7968-7975.
[13] Wei, N., X. Li, Z. Fang, B. Bai, Q. Li, S. Liu, and Y. Jia. 2015. Regional resource distribution of onshore carbon geological utilization in China. *Journal of CO_2 Utilization*, 11, 20-30.
[14] Van-Dal, É. S. and C. Bouallou. 2012. CO_2 abatement through a methanol production process. *Chemical Engineering Transactions*, 29, 463-468.
[15] Yadav, V. S., M. Prasad, J. Khan, S. S. Amritphale, M. Singh, and C. B. Raju. 2010. Sequestration of carbon dioxide (CO_2) using red mud. *J Hazard Mater* 176(1-3): 1044-1050.
[16] Huijgen, W. J., G.-J. Witkamp, and R. N. Comans, 2005. Mineral CO2 sequestration by steel slag carbonation. *Environmental science & technology* 39(24): 9676-9682.
[17] El-Hassan, H. and Y. Shao. 2014. Carbon Storage through Concrete Block Carbonation. *Journal of Clean Energy Technologies*: 287-291.
[18] Hignett, T. P. 1985. *Fertilizer manual*: Martinus Nijhoff/Dr. W. Junk Publishers.
[19] Blom, T.J; Straver, W.A.; Ingratta, F.J.; Shalin Khosla, 2009. Carbon Dioxide in Greenhouses. Available at: http://www.omafra.gov.on.ca/english/crops/facts/00-077.htm/ [Accessed 10/11/ 2015].

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Surrounding planting and its effect on the energy balance at a zero energy demand building

A. Moumtzakis, P. Kosmopoulos*, S. Zoras

Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements,
Democritus University of Thrace, 67100, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

This paper examines the proper planting order and the use of evergreen and deciduous trees for shading the surrounding area and the structure elements of a building, in order to achieve thermal comfort conditions for the inhabitants, through the energy balance aiming at a Zero Demand Building. The simulation project takes place at a northern city of Greece, Thessaloniki (G. Lat. 40.23˚ – G. Long. 23.00˚). Main objective of this study is the development of a calculation procedure which can be used from designers in order to calculate the height of planting in relation with the distance from the building. The plan of proper planting uses the solar movement, radiation, and Heating /Cooling Degree Days to build a shade zone for summer and a sun zone for winter based on bioclimatic design principles. The aim of the analysis is to point out that large amount of energy can be saved by using several "green" techniques and criteria in order to reduce the environmental footprint of cities in the area of South Europe.

Keywords: energy balance; proper planting; Zero Energy Building; bioclimatic design.

1. INTRODUCTION

The European Union is facing a variety of energy challenges resulting from energy scarcity, large amounts of energy imports, increasing of energy consumption and because of its policy adaptations to limit climate change. A significant part for a future solution will be the energy efficiency policies for buildings and environment. In accordance with Directive 2010/31/EU of the European parliament and of the council of 19 May 2010 on the energy performance of buildings 40% of total energy consumption has its origin in public and private buildings [1]. It is obvious that energy savings should be a priority for a sustainable living. Bioclimatic criteria and ecological techniques used to form the proper conditions between the environment and constructions [2]. Thus, the contribution of planting affects the microenvironment as a regulatory factor around the building through shading and evapotranspiration phenomenon, the energy balance is affected also by the periodic changes of the sun during the summer season and by the appropriate planting design. The heat transfer phenomenon increases through the construction materials as the sun's heat energy is absorbed into the wall, therefore a comfort zone is necessary at achieving a sustainable design. The appropriate position (azimuth, 0˚-360˚) for a tree in relation with a distance from a building giving the proper height creating a physical obstacle which in combination with sunshade reduces the amount of energy for cooling in summer season.

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2. MATERIALS AND METHODS

The objective of the present work is to examine the weather conditions at the study location and specifically the cooling load during summer period and analyse how the proper planting type should be designed to succeed thermal comfort conditions and comfort indices like PMV-PET-SET [3,4]. Both graphs in Figure 1 and 2 show the average daily per month solar radiation, heating and cooling degree days and Minimum, Maximum, Average temperatures per month [5,6]. Calculations with sophisticated programs like Energy Plus, Ecotect analysis, Meteonorm, 3d Studio Max using weather data for making the simulation process more accurate. The 3d model analyzing the environmental plan around the building and calculates in combination with weather data base the cooling loads for summer, which are very important for shade zone and the type of construction at any place according to bioclimatic architecture. Analytically, both diagrams represent the load of cooling and heating for a specific region, equations below calculate the sun path and give the correct angle (a) as it seen in Figure 3. Main purpose of this paper is to identify with accuracy the height of planting, the coordinates for the right position (azimuth) and the cooling energy KWh/m^2 for a variety of window sizes.

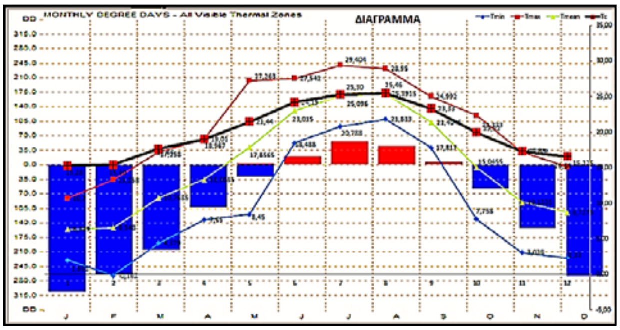


Figure 1: Representation of H/CDDs and limits of comfort.

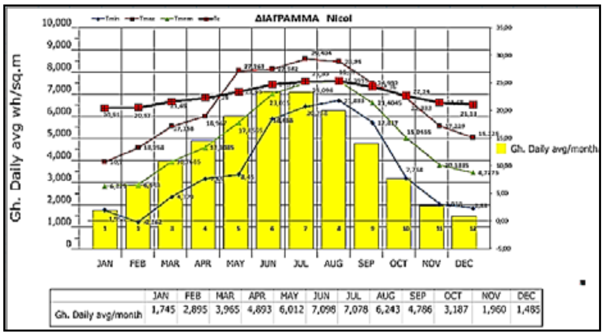


Figure 2: Representation of temperatures and comfort levels.

2.1 Geometric method for solar path and height of planting

The periodic changes of the sun produce a variety of energy amount which is a result of sun's elevation and the azimuth. The equations below give the specific position of the sun for any day and time in the year and also the angle which calculates the triangle for the height of the tree in order to design an excellent shade zone at any side of the building.

Day of the year:

$$D_y = D_1 + D_2 + D_X \quad (1)$$

Solar declination according to (Smith and Wilson 1976) is given by:

$$\boldsymbol{\delta = 23.45^\circ \sin\left(\frac{360^\circ\,(D_y - 81)}{365}\right)} \quad (2)$$

In radians according to (Pier point 1982):

$$\delta = 0.4093 \sin\left(\frac{2\pi\,(D_y - 81)}{365}\right) \quad (3)$$

The solar time is given as follows:

$$S.T. = L.T. \pm 4\left(L_t - L_{ong.}\right) + E_t$$

(4)

Equation of time is given by:

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$$E_t = 229.2(0.000075 + 0.001868\cos(B) - 0.032077 sin(B) \\ -0.014615\cos(2B) - 0.04089\sin(2B)) \quad (5)$$

where B is the coefficient of equation of time:

$$B = (D-1)\frac{360}{365} \quad (6)$$

L_t is the standard meridian for the local time zone, L_{ong} is the longitude of the location. The hourly declination angle of the sun is given by the relation:

$$w = 15^{\circ}(12 - S.T.)\ \ \gamma\iota\alpha\ \ S.T.12 \quad (7)$$

$$w = 15^{\circ}(S.T. - 12)\ \ \ \gamma\iota\alpha\ \ S.T. > 12 \quad (8)$$

$$\text{or}\ \ w = 15^{\circ}\,|S.T. - 12| \quad (9)$$

Solar elevation angle calculated from the relationship (Kittler and Mikler (1986) :

$$a = sin^{-1}(cos\varphi * cos\delta * cos\omega + sin\varphi * sin\delta) \quad (10)$$

Solar azimuth angle calculated from the relationship:

For morning hours, H $\leq$ 12

$$cosA_S^N = cotA_S^N\ sinA_S^N$$

$$= \frac{1}{sin\omega}\ (\cos\varphi\ tan\delta + sin\varphi\ cos\omega)\frac{cos\delta\ sin\omega}{cosa}$$

$$= \frac{cos\delta}{cosa}\ (\cos\varphi\ tan\delta + sin\varphi\ cos\omega)$$

$$= \frac{1}{cosa}\ [(\cos\varphi\ sin\delta + sin\varphi\ cos\delta\cos\ (15^{\circ}\ H)] \quad (11)$$

Then afternoon azimuth for H $>$ 12   can be calculated after:

$$cosA_S^N = 360^{\circ} - \frac{1}{cosa}\ [(cos\ \varphi\ sin\delta + sin\varphi\ cos\delta\ cos\ (15^{\circ}\ H)] \quad (12)$$

Angle for ENa triangle:

$$N = 180 - 90 - a \quad (14)$$

Side n for triangle ENa calculated from the law sines:

$$\frac{e}{E} = \frac{n}{N} = \frac{c}{a} \quad (15)$$

Side for ABa triangle:

$$b = x + n \quad (16)$$

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Side y (height of the planting) for triangle Aba calculated from the law sines:

$$\frac{t}{A} = \frac{b}{B} = \frac{y}{a} \qquad (17)$$

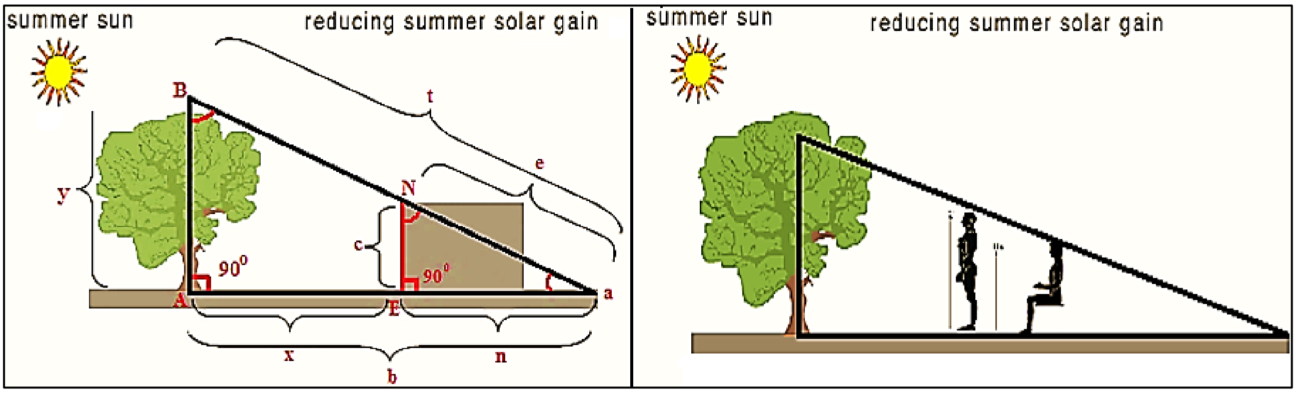


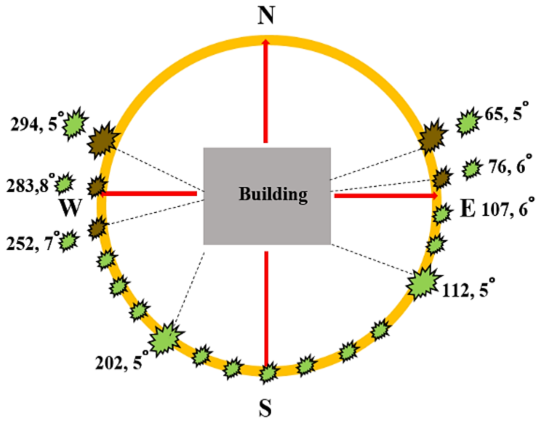
Figure 3: Geometric study of the solar gain

2.2 Appropriate Planting and combination with sunshade elements

Winter season in the N. Hemisphere (G. Latitude 40, 5 ˚ - G. Longitude 23 ˚) includes the following months December – January – February. The winter period ends on 28 of February, during the winter months solar radiation is acceptable because sun increases thermal gains and improves energy balance. On February 28, the sunrise starts at 07:06 a.m. and 100.3˚ azimuthal angle and sun sets at 18:16 p.m. with azimuthal angle 259.9˚. In accordance with General Building Regulation [8], there is acceptable insolation when the sun's elevation is over 7.5˚ and the azimuthal angle 22.5˚ from the study surface, thus the acceptable energy from the sun starts at 07:50 a.m. with **107.6 ˚**azimuthal angle and elevation angle 7.7˚ and lasts until 17:32 p.m. elevation angle 7.7˚ with azimuthal angle **252.7˚**, Figure 4 and 5. Using the specific position for planting design, a solar window remains open for solar radiation and the sun rays are not blocked by anything, thus the sun radiation comes into the building. Analytically as it seen in Figure 4 and 5, the plan includes two options, the first one which starts from 107.6˚ azimuthal angle and the first type of vegetation belong to the category of deciduous trees which ends at 252.7˚ azimuthal angle Figure 4, and the second one in which the planting combines with sun protection elements (sunshades). It is obvious that in the Figure 5 there is sun protection with sunshades, so there is no deciduous trees in the south side of the building.

The summer season includes June - July and August, On June 21th each year, the rays of the sun will be perpendicular to the Tropic of Cancer at 23°30' North latitude. This day is the summer solstice in the Northern Hemisphere. The sun rises earliest in the morning and it sets latest at night, thereby the energy load is higher and the need for cooling maximizes as it seen in Figure 1 and 2. At the study area on June 21th the sunrises at 05:00 a.m. with azimuthal angle 58.0˚. It is mentioned above that the acceptable insolation is when the sun's elevation is over 7.5˚ and the azimuthal angle 22.5˚ from the study surface, thus the acceptable energy from the sun starts at 05:48 a.m. with **65.5˚** azimuthal angle and elevation angle 7.6˚ and lasts until 19:12 p.m. elevation angle 7.6˚ with azimuthal angle **294.5 ˚**, Figure 4 and 5. The proper placement which have already been referred blocking the sun rays when the sun rises (65.5 azimuthal angle) and later when the sun sets at north west of the building (294.5˚ azimuthal angle) at this point it is important to refer that it can be used both types of vegetation evergreen (dark green) or deciduous (light green), Figure 4 and 5, in combination with wind maps and their strategic use on the field.

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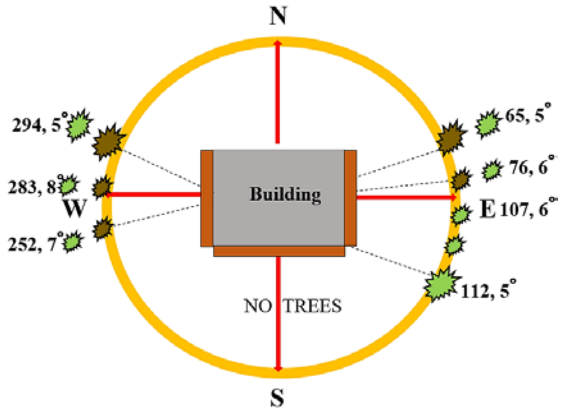


Figure 4: Appropriate planting around the building without sun shades.

Figure 5: Appropriate planting around the building with sun shades.

The spring season includes the months March - April - May, according to, May is the month in which begins the trend of high temperatures which exceed the comfort zone that is set for this study area (G. Latitude 40, 5° - G. Longitude 23°), and is also observed and the onset of Cooling Degree Days. So that, is the month in which proper routes of planting and use of evergreen and deciduous trees have been made in order to shade the surrounding area , the building and thus to succeed thermal comfort of the people who live there. However, the months of March and April respectively maintain low temperatures (9.5 °C - 13.2 °C), hence the first type of vegetation belongs to the category of deciduous, so it allows passage of the solar rays from the southeast and southwest openings during the Spring season for keeping solar gains in balance with losses. At the study area on May 1th the sunrises at 05:29 a.m. with azimuthal angle 69.5°and sun sets at 19:22 p.m. with azimuthal angle 290.8. It is mentioned above that the acceptable insolation is when the sun's elevation is over 7.5° and the azimuthal angle 22.5° from the study surface, thus the acceptable energy from the sun starts at 06:14 a.m. with **76.6**° azimuthal angle and elevation angle 7.7° and lasts until 18:38 p.m. elevation angle 7.7° with azimuthal angle **283.8**°, Figure 4 and 5.

Table 1. Appropriate planting in combination with sunshades

Altitude of the Sun , Jun 21, 2016 Azimuth of the Sun , Jun 21, 2016 **E 23 00, N40 23**			West Site of The Building		West Site of The Building		West Site of The Building		West Site of The Building	
			Height of the planting (y), at a distance 5 and 3 meters from the building (m)							
Zone: + 2h East of Greenwich Thessaloniki			Without Sunshade		0.60 m Sunshade		1.00 m Sunshade		1.50 m Sunshade	
Local Time	Solar Altitude	Solar Azimuth	5m	3m	5m	3m	5m	3m	5m	3m
12:59	72	202.5	18.4	12.2	-	-	-	-	-	-
13:59	64.7	234.6	13.6	9.35	11.98	7.75	10.98	6.75	-	-
14:59	54.5	253	10	7.2	9.11	6.31	8.54	5.74	7.81	5
15:59	43.3	265.2	7.7	6	7.14	5.26	6.77	4.89	6.3	4.41
16:59	30.7	275	6	4.8	5.61	4.42	5.38	4.19	5.5	3.88
17:59	20.6	283.8	5	4	4.65	3.90	4.49	3.74	4.3	3.55
18:59	9.8	292.6	4	3.5	3.75	3.41	3.66	3.32	3.6	3.2

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As it is shown in Table 1, have been made four simulations for western side of the building which is the most sensitive surface because of the energy loads during the summer period. The simulation estimates on the combination between the vegetation and the sunshades. The sunshade model has three types of length, 1.5m – 1.0m – 0.6m, in combination with appropriate planting position (azimuthal angle) and its distance 3m - 5m from the building. The height of the tree is the key for the correct type of planting. Information that is presented in Table 1, compares the types of planting and the use of sun protection elements in order to contribute at the energy balance of the building.

3. RESULTS AND DISCUSSION

3.1 Effect of appropriate planting

The analysis of proper planting which have been created and placed in the surroundings created a map of energy that develops around the building. The appropriate planting form creates a "ring" of shade around the building and protects the surrounding area from the amount of energy which is obviously reduced as it is illustrated in Figure 6, 7, 8 and 9. Construction elements including Walls, Columns, Beams, etc. absorb less energy by the sun.



Figure 6: Appropriate planting.

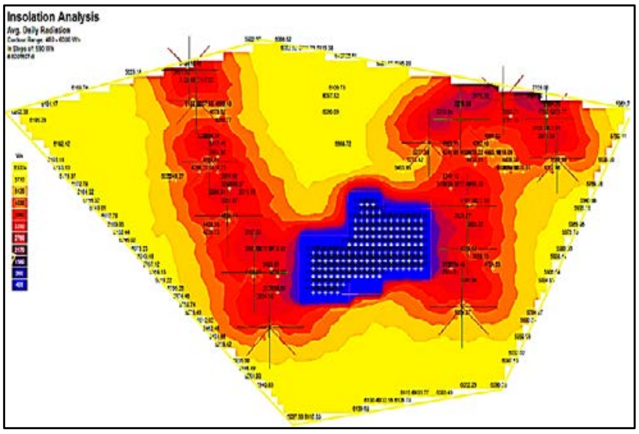


Figure 7: Amount of energy around the building.

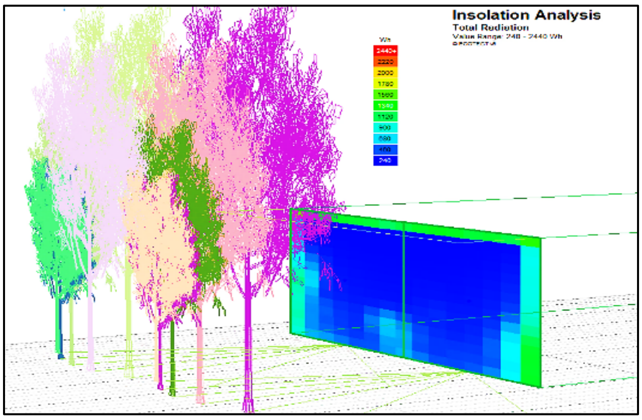


Figure 8: Shade zone on June 21th.

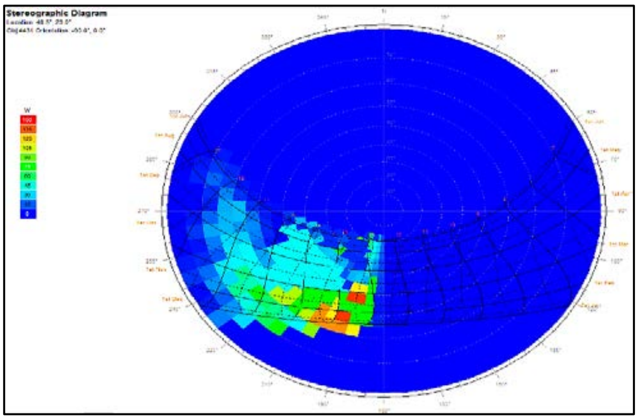


Figure 9: Amount of energy on June 21th

The simulation which has been made at the western part of the building, Figure 8 and 9, indicates less radiation per square meter at the study surface in the 87.5% of the total area. The

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87.5% has very low rates of energy at the center of the surface and the 2.5% of the surface a bit increased close to the sides of the study area. The energy balance is affected especially when the surface has a window, Figure 10, 11 and 12. The stereographic diagram Figure 9, for energy loads (watts) represents the solar path during the year and solar radiation for the study area (Western side of the building). Main objective is to identify if the sun rays and the amount of their energy is allowed in winter and if not in the summer season, according to the plan of appropriate vegetation. Analytically in the Figure 9 the diagram illustrates that the winter zone uses the sun rays for heating the inhabitants and blocks them in summer season.

3.2 Thermal comfort indices

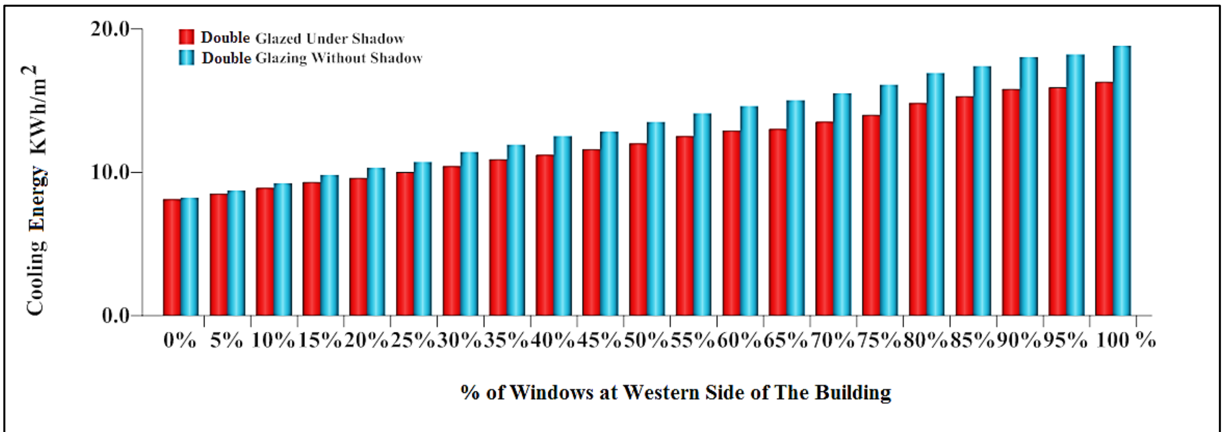
The western section was also studied during the summer season with the software RayMAN [5], the indicators (PMV, PET and SET) of thermal comfort [3, 4] have been examined outdoors in the west side of the building at 15:00 p.m.

Table 2. Thermal Comfort Indices.

Thermal Comfort Indices – Western Side of the Building – 15:00 p.m.				
Period	Winter season			
Project Thermal Comfort	Without trees on the field	Human sensation	With trees on the field	Human sensation
Seat	PMV -3,0 PET -5,5 SET 0,0	Cold Very cold Very cold	PMV -3,6 PET -4,9 SET -3,8	Very cold Very cold Very cold
Walk	PMV -2,2 PET 1,0 SET 5,0	Cold Very cold Very cold	PMV -3,0 PET -4,9 SET 6,3	Cold Very cold Very cold
Period	Summer season			
Project Thermal Comfort	Without trees on the field	Human sensation	With trees on the field	Human sensation
Seat	PMV 2,9 PET 30,4 SET 26,9	Hot Hot Slightly warm	PMV 0,3 PET 22,3 SET 14,8	Comfortable Slightly cool Cool
Walk	PMV 3,2 PET 36,6 SET 28,9	Very Hot Hot Slightly warm	PMV 1,9 PET 28,7 SET 21,2	Warm Warm Slightly cool

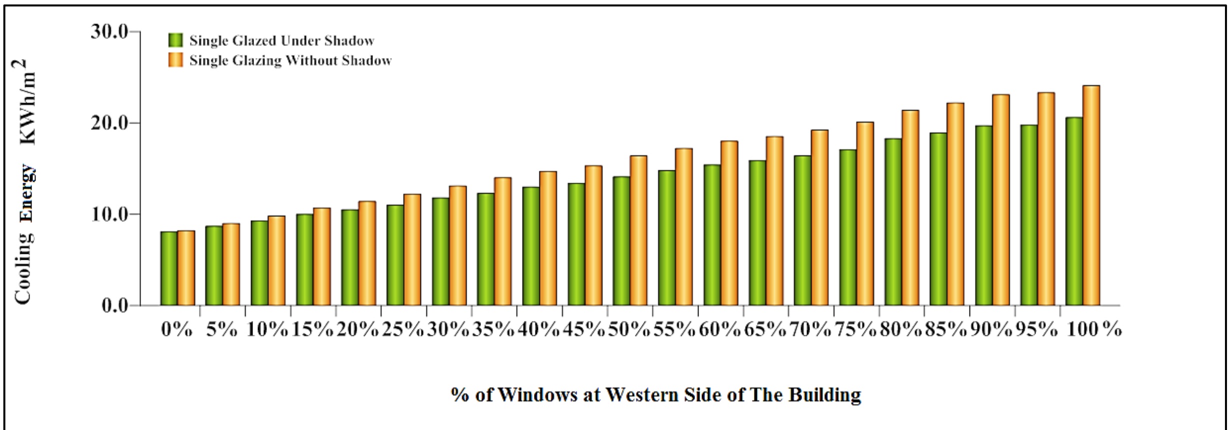
Thermal comfort conditions have been calculated for winter season and summer season with an average of temperatures at the study region. The human body examined in two different activities for a walking person and another one for a seated man. In combination with appropriate vegetation (deciduous, evergreen) the Rayman software examines the human sensation for the study area, Table 2. Analytically, as it is shown in Table 2, in winter season the human sensation is in a better condition without trees on the field with the sun over the study area without obstacles, than a scenario with trees on the field. This is a result of reduced energy through shading and evapotranspiration phenomenon. In the summer season thermal comfort indices are excellent for the scenario with appropriate planting design and not acceptable for the scenario without vegetation.

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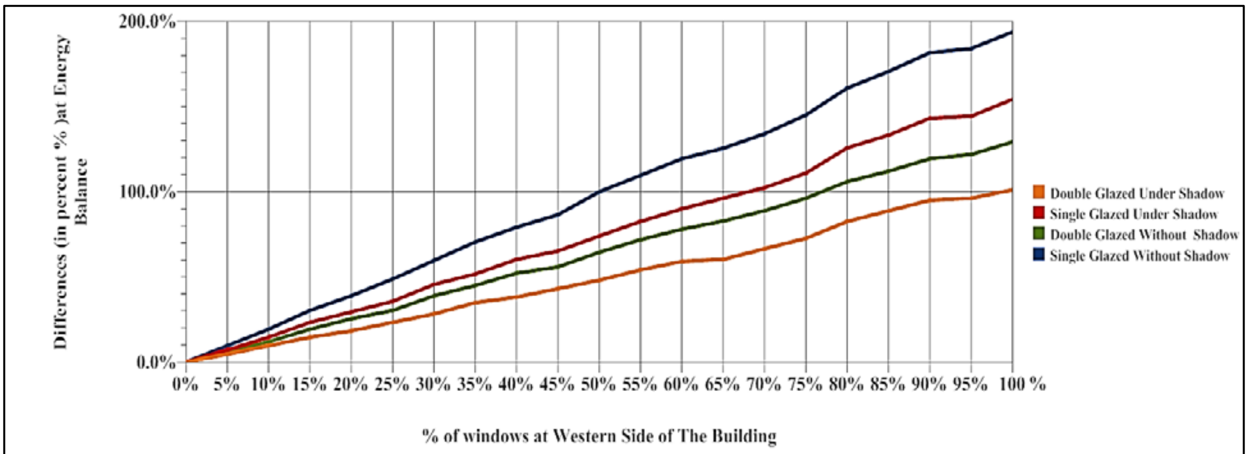
	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	95%	100%
Double Glazed Under Shadow	8.1	8.5	8.9	9.3	9.6	10.0	10.4	10.9	11.2	11.6	12.0	12.5	12.9	13.0	13.5	14.0	14.8	15.3	15.8	15.9	16.3
Double Glazing Without Shadow	8.2	8.7	9.2	9.8	10.3	10.7	11.4	11.9	12.5	12.8	13.5	14.1	14.6	15.0	15.5	16.1	16.9	17.4	18.0	18.2	18.8

Figure 10: Cooling energy KWh/m^2 for a different size of a window (double glazed) at western side.



	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	95%	100%
Single Glazed Under Shadow	8.1	8.7	9.3	10.0	10.5	11.0	11.8	12.3	13.0	13.4	14.1	14.8	15.4	15.9	16.4	17.1	18.3	18.9	19.7	19.8	20.6
Single Glazing Without Shadow	8.2	9.0	9.8	10.7	11.4	12.2	13.1	14.0	14.7	15.3	16.4	17.2	18.0	18.5	19.2	20.1	21.4	22.2	23.1	23.3	24.1

Figure 11: Cooling energy KWh/m^2 for a different size of a window (single glazed) at western side.



	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	95%	100%
Double Glazed Under Shadow	0.0%	4.9%	9.9%	14.8%	18.5%	23.5%	28.4%	35.0%	38.3%	43.2%	48.2%	54.3%	59.3%	60.5%	66.7%	72.8%	82.7%	88.9%	95.1%	96.3%	101.2%
Single Glazed Under Shadow	0.0%	7.4%	14.8%	23.5%	29.6%	35.8%	45.7%	51.9%	60.5%	65.4%	74.1%	82.7%	90.1%	96.3%	102.5%	111.1%	125.9%	133.3%	143.2%	144.4%	154.3%
Double Glazed Without Shadow	0.0%	6.1%	12.2%	19.5%	25.6%	30.5%	39.0%	45.1%	52.4%	56.1%	64.6%	72.0%	78.1%	82.9%	89.0%	96.3%	106.1%	112.2%	119.5%	122.0%	129.3%
Single Glazed Without Shadow	0.0%	9.8%	19.5%	30.5%	39.0%	48.9%	59.8%	70.7%	79.3%	86.6%	100.0%	109.8%	119.5%	125.6%	134.1%	145.1%	161.0%	170.7%	181.7%	184.1%	193.9%

Figure 12: Differences at energy balance with different window sizes.

3.3 Effect of appropriate planting on the energy balance of a building

The western part of a building is quite sensitive to high temperatures in summer, the proper planting design is an important factor for the bioclimatic architecture. The combination amongst the vegetation and the energy balance is a significant part of this work, the simulation which has been done indicates how a building model reacts. The basic properties of the building elements include, X-Y-Z, 12m-8m-3m, dimensions of the building, total floor area: 96.00 m^2, surface area: 312.00 m^2, exposed area: 216.00 m^2, masonry wall: U-value 0.45 W/m^2K, typical floor: U-value 0.80 W/m^2K, and roof: U-value 0.40 W/m^2K, the window at the first scenario has double glazed and U-value 2.2 W/m^2K, and for the second part of the simulation single glazed and U-value 6.0 W/m^2K. The analysis took place in summer period at 13:00 p.m. - 19:00 p.m. when the sun was moving at the western part of the building. The only window is at the western surface and analyzes different sizes during the simulation in order to calculate the energy balance in correlation with the size of a window. As it is presented in Figure 10, 11 and 12, it is obvious the relation between the energy balance, the type of the openings and the shade zone. The cooling energy increases while changing the size of the window in addition, the energy needs are increased in relation with shade zone analysis and the type of the glazed system.

4. CONCLUSIONS

The project which has been scheduled for the region of Thessaloniki, indicates how effective can be the design of a building or an outdoor space in accordance with bioclimatic principles. The necessity for reduced amount of energy uses "green" techniques to improve the energy balance and thermal comfort indices (PMV-PET-SET). It is obvious that the study of the weather data in the region, the appropriate vegetation and the proper window size with sun protection elements define the reactions between the construction and the environmental parameters. Cooling energy and thermal comfort indices depending on holistic design of the surroundings, having a right option of a window type (double, single) and proper size according to the surface study can be achieved energy balance during the summer season and energy savings throughout the year. The cooling energy per square meter can be increased at 193, 9% of the energy balance using a large size of a window with not good U-value or could have a lower cooling energy value using a smaller size.

References

[1] Council Directive 2010/31/EU of 19 May 2010 *on the energy performance of buildings* [2010] OJ L153/13, p1 para 3.

[2] Kosmopoulos P., 2008. *Energy and the Environment: Less energy demand, less emissions, in Buildings*. 1st Ed. University Studio Press, Thessaloniki.

[3] Matzarakis A., Rutz F., Mayer H., 2007. Modelling radiation fluxes in simple and complex environments—application of the RayMan model. *International Journal of Biometeorology*, 51:323–334 DOI 10.1007/s00484-006-0061-8.

[4] Yea G., Yangaa C., Chenaa Y., Yuguo Lib., 2003.A new approach for measuring predicted mean vote (PMV) and standard effective temperature (SET*), *Building and Environment* **38**, 33 – 44.

[5] Mourshed M., 2012. Relationship between annual mean temperature and degree-days, *Energy and Buildings* **54**, 418–425.

[6] Humphreys M.A. Rijal H.B. Nicol J.F. Updating the adaptive relation between climate and comfort indoors; new insights and an extended database. Building and Environment 63, 40e55.

[7] Kittler R., Darula S., 2008b. Historicka´ doˆ lezˇitostˇ sola´rnej geometrie preorienta´ciu v cˇase, priestore a v architecture. (In Slovak: Historical importance of solar geometry for the orientation in time and space and in architecture), *Architektu´ra & urbanizmus* **42**, 3–4, 159–165.

[8] Tzonos P., 1985. *Insolation*. Observer Studio Press Thessaloniki.

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Focusing solar spectrum by anthracene molecules

L. J. Liu*, T. Cao

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
*Corresponding author: Email: liulj@whu.edu.cn

Abstract

UV and NIR portions of Xenon light-simulated solar spectrum are focused into visible light with maximum wavelengths ranging from 415 to 471 nm through the two-way photoluminescence of three anthracenes, anthracene (AN), fluoranthene (FLA) and 9,10-diphenylanthracene (DPA), and the intensity of the visible light is two times as that of excitation lights.

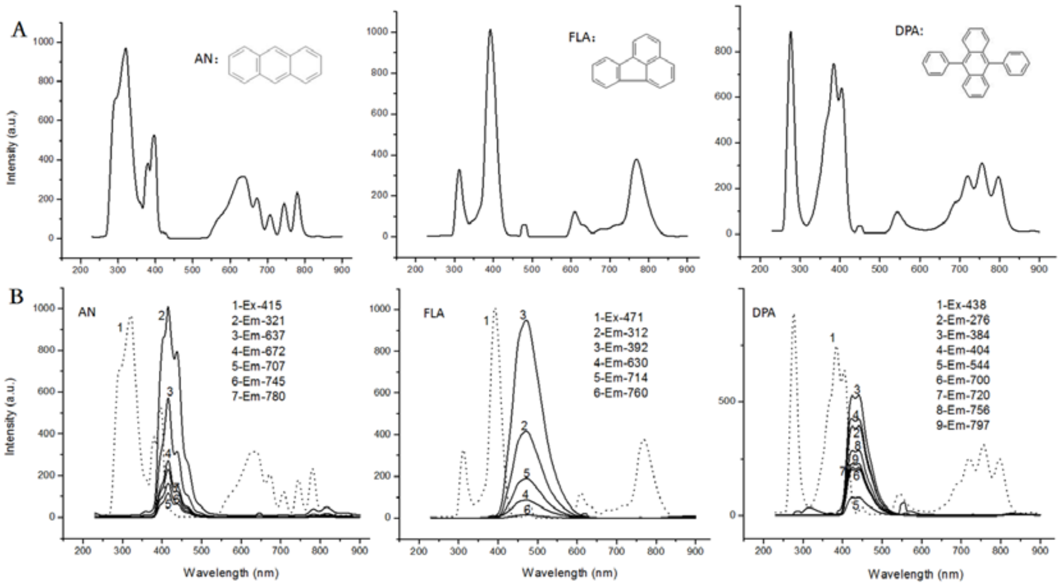
Keywords: focusing; solar spectrum; two-way conversion; anthracene

Focusing UV and IR portions of sunlight in the visible spectral region and then transforming the visible light into power or hydrogen is a more economical and more convenient substitute for directly harvesting them as the visible portion of sunlight is the light source of light-catalyzed water split into hydrogen, dye-sensitized solar cells, organic solar cell, thin-film silicon solar cell as well as industrial solar cell. Using this approach, the efficiency of solar energy is significantly enhanced with the increased intensity of the visible portion of sunlight. The conversion of UV and IR light into visible light is two-way photoluminescence (down-/up-conversion, DC/UC) and the conversion of IR light into visible light should be excited by a monochromatic laser. On the other hand, DC and UC usually are two independent processes and the united devices/systems of DC/UC are complex, and their preparations are cumbersome. Wavelength-focused (WF) molecules are such molecules that are able to shift the portions of shorter and longer wavelengths of incident light into an identical wavelength in between, by which polychromatic light is converted into monochromatic light. Recently, we synthesized some WF monofluorophore organic molecules that not only are stimulated by two or more monochromic UV and NIR portions of a Xenon light source but also emit visible light at an identical wavelength, which inspires us to find more WF molecules from the well-known fluorescent dyes that all emit much stronger fluorescence. We present in this paper that solar spectrum can be focused by anthracene (AN), fluoranthene (FLA) and 9,10-diphenyl-anthracene (DPA).

The excitation and fluorescence spectra of the anthracenes were recorded on a Shimadzu RF-5301PC spectrofluorophotometer scanning from 200 nm to 900 nm. Figure 1A shows that the three anthracenes can all be stimulated by either polychromatic UV light or polychromatic NIR light, indicating that the potions of sunlight at these wavelengths are potentially converted by the anthracenec through their photofluoscence.

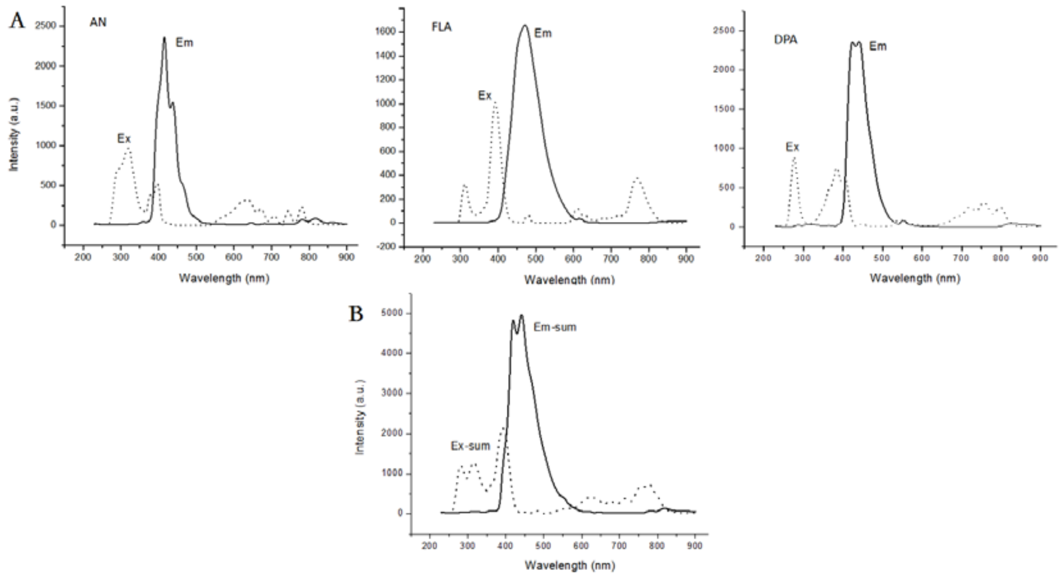
It is recorded that the maximum emitted wavelengths of each anthracene by various excitation wavelengths are nearly the same, and that for AN, FLA and DPA is around 415, 471 and 438 nm, respectively (Figure 1B). However, the excitation wavelengths of the three anthracenes sit at two bands: shorter or longer than the emitted wavelengths, showing that the UV and NIR portions of sunlight at the excitation wavelengths are focused together at their emitted wavelengths. The focused spectra of the anthracenes are presented in Figure 2A. The advantage of the mixture of AN, FLA and DPA is that the weak NIR light can be utilized as part of the energy source to make the strong visible light (Figure 2B).

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A: Excitation spectra of anthracenes,
B: Emission spectra of anthracenes with various excitation wavelengths

Figure 1 Excitation and emission spectra of anthracenes



A: Each of anthracenes, **B**: Mixture of AN, FLA and DPA

Figure 2 Focused spectra of anthracenes

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References

[1] Jia X.X., Li Y., Wu J., Chen C., Liu L.J., 2015, One-pot catalyst-free synthesis of down- and upconversion fluorescent oligopyrazolines from diazoacetates and maleic anhydride. *Polymer Chemistry*, **6**, 4071-4079.

[2] Li F.F., Xiao L.Q., Li Y., Chen C., Liu L.J., 2015, The interception of a copper-based carbene radical with an α-carbonyl diazomethane radical: C1/C1N2 copolymerization. *Chemical Communications*, **51**, 11964-11967.

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Evaluation of rainfall time series by statistical methods

M. Zeleňáková[1*], I. Alkhalaf[1], P. Purcz[1], P. Blistan[2], M. M. Portela[3]

[1] Department of Environmental Engineering, Technical University of Košice, Košice, Slovakia.
[2] Institute of Geodesy, Cartography and Geographical Information Systems, Technical University of Košice, Košice, Slovakia.
[3] Department of Civil Engineering, National Technical University of Lisbon, Lisbon, Portugal.
*Corresponding author: Email: martina.zelenakova@tuke.sk

Abstract

Most of the recent studies about climate change suggest that the behaviour of some of the climatological variables has already changed and will continue to change towards increasing or decreasing magnitudes and frequencies, depending on the type of variable. Increased rainfall and floods are expected in some regions while other regions will experience smaller rainfall and longer droughts, meaning water scarcity. The Mann-Kendall test coupled with the Sen's slope was applied to identity the significant trends, as well as the increasing or decreasing trend and the magnitude of those trends. The results achieved for rainfall are revealed more frequent significant decreasing trends. The Intergovernmental Panel on Climatic Change`s (IPCC) Fifth Assessment Report concluded that precipitation has generally increased over latitudes north of 30 over the period of 1900–2005 and decrease in the Mediterranean and southern Asia. In the presented paper we evaluate out coincidence with the IPCC report – decreasing rainfall in Syria.

Keywords: Mann Kendall test; trend analysis; precipitation

1. INTRODUCTION

The Intergovernmental Panel on Climate Change [1] provides a comprehensive review of the potential impacts on climate. Climatic change is considered likely to increase runoff in the higher latitude regions because of increased precipitation on the other hand flood frequencies are expected to change also in some locations and the severity of drought events could increase as a result of those changes in both precipitation and evaporation. In all these considerations 'the issue' then becomes the effect of global warming and its impacts on the environment and water resources in particular. Precipitation is one of the most important variables for climate and hydro-meteorology. Changes in precipitation pattern may lead to floods, droughts, loss of biodiversity and agricultural productivity. Therefore, the spatial and temporal trends of precipitation results are important for climate analyst and water resources planner [2,3]. Precipitation has changed worldwide during the last decades mainly due to climate variability. Climate change studies have demonstrated that the land-surface precipitation shows an increase of 0.5–1% per decade in most of the Northern Hemisphere mid and high latitudes, and annual average of regional precipitation increased 7–12% for the areas in 30–85° N and by about 2% for the areas 0°–55° S over the 20th century [4,5].

Many researchers have given a great deal of attention to the potential impacts of climatic change and variability in several fields at international level. Only some of them have investigated the rainfall variability in Southeast Asia. For instance, Endo et al. (2009) [6] investigated trends in extreme precipitation using almost the entire network of stations in Southeast Asia. Almazroui et al. [7,8] gave insight into the recent, past and present climate as well as climate change in the Arabian Peninsula, in particular over Saudi Arabia. The Middle East countries, including those on the

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Arabian Peninsula, are characterized by large variations in their climatic conditions, and these variations can be significant within a single country (Ragab and Prudhomme, 2000) [9]. Some studies in Iran have examined the changes in meteorological variables [10,11]. In contrary their results showed that there was no statistically significant climate variability or only slightly decreasing trend in annual precipitation in Iran. Almost no study is devoted to rainfalls trend or climate variability and its impact to water resources (to the best authors' knowledge) in Syria.

Rainfall is a critical meteorological parameter and needs to be measured and evaluated accurately; many applications of rainfall data can be studied in depth through knowledge of the actual distribution of rainfall. Additionally, the amount of rainfall received over an area is an important factor in assessing the amount of water available to meet the various demands of agriculture, industry, and other human activities [7]. This paper investigate rainfall trends over all Syria. Data for evaluation were obtained from Aleppo University in Syria with collaboration of Ministry of Agriculture and Agrarian Reform and Meteorological Center in Syria. The evaluated period is from 1992 to 2010.

2. MATERIALS AND METHODS

2.1 Study area

Syria is a country in the Middle East (Figure 1.), bordering the Mediterranean Sea between Lebanon and Turkey. The area of Syria is 185,180 km². Terrain is narrow coastal plain with a double mountain belt in the west; large, semiarid and desert plateau to the east. Climate is mostly desert; it has hot, dry, sunny summers (from June to August) and mild, rainy winters (December to February) along coast [12].

It is important to evaluate how climate has varied and changed in the past. The monthly mean historical rainfall and temperature data can be mapped to show the baseline climate and seasonality by month, for specific years, and for rainfall and temperature.

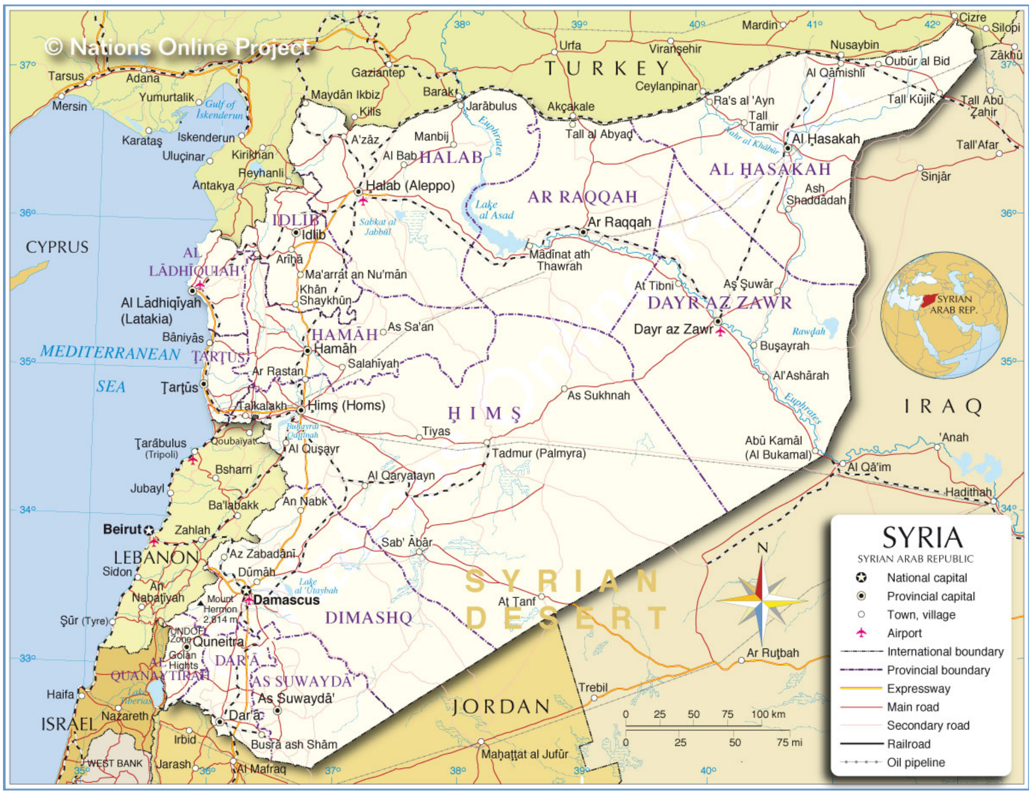


Figure 1. Study area [12]

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The chart below (Figure 2.) shows mean historical monthly temperature and rainfall for Syrian Arab Republic during the time period 1900-2012. The dataset was produced by the Climatic Research Unit of University of East Anglia [12].

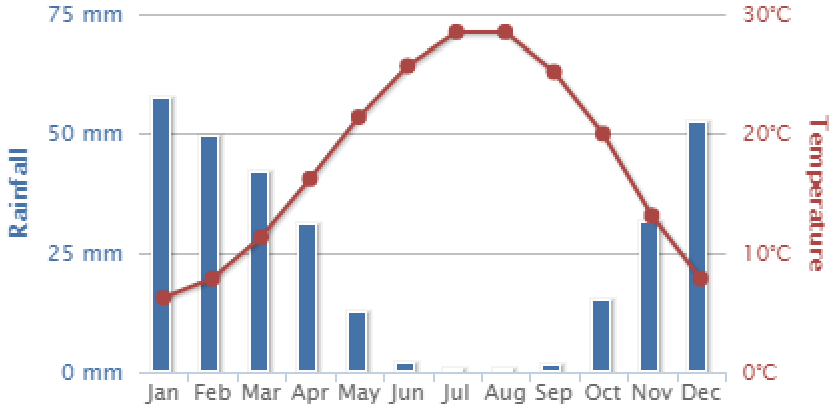


Figure 2. Average monthly temperature and rainfall for Syrian Arab Republic from 1900-2012 [13]

2.1 Statistical analysis

In this study non-parametric Mann-Kendall test is used for the detection of the trend in a time series. Mann-Kendall test [14,15] is following statistics based on standard normal distribution (Z), by using Eq. (1).

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}} & if \quad S > 0 \\ 0 & if \quad S = 0 \\ \frac{S+1}{\sqrt{Var(S)}} & if \quad S < 0 \end{cases} \tag{1}$$

in which,

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \; sgn(x_j - x_k) \tag{2}$$

$$sgn(x_j - x_k) = \begin{cases} +1 & if \left(x_j - x_k\right) > 0 \\ 0 & if \left(x_j - x_k\right) = 0 \\ -1 & if \left(x_j - x_k\right) < 0 \end{cases} \tag{3}$$

$$Var(S) = [n(n-1)(2n+5) - \sum_{i=1}^{m} t_i(t_i - 1)(2t_i + 5)]/18 \tag{4}$$

where n is the number of data points, m is the number of tied groups (a set of sample data having the same value).

According to this test, the null hypothesis H0 states that the depersonalized data ($x_1, \ldots, x_n$) is a sample of n independent and identically distributed random variables. The alternative hypothesis H1 of a two-sided test is that the distributions of x_k and x_j are not identical for all $k, j \leq n$ with $k \neq j$. The significance level is chosen as $\alpha = 0.05$ and $Z_{\alpha/2}$ is the value of normal distribution function, in this case $Z_{\alpha/2} = 1.95996$. Hypothesis H0 - no trend is if ($Z < Z_{\alpha/2}$) and H1 - there is a trend if $Z > Z_{\alpha/2}$. Positive values of Z indicate increasing trends, while negative values of Z show decreasing trends.

The magnitude of the trend was determined using Sen`s estimator. Sen's method assumes a linear trend in the time series and has been widely used for determining the magnitude of trend in hydro-meteorological time series e.g. [16,17,18,19,20]. In this method, the slopes (β) of all data pairs are first calculated by

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$$\beta = Median\left((x_j - x_k)/(j - k)\right) \quad (5)$$

for i = 1, 2, ..., N,.where x_j and x_k are data values at time j and k ($j > k$), respectively and N is a number of all pairs x_j and x_k. A positive value of β indicates an upward (increasing) trend and a negative value indicates a downward (decreasing) trend in the time series.

All mathematical relationships (1), (2), (3), (4) and (5) were programmed in Visual Basic in Microsoft Excel 2003.

3. RESULTS AND DISCUSSION

Results of rainfall analysis – annual trends are presented in Table 1 for monthly average data. Monthly data series for the 19 years period, from 1992-2010, were considered for trend detection. The evaluation was done for the time period from October to May (X – V) as rainfall in other months was almost zero. Bold values indicate statistical significance at 95% confidence level as per the Mann–Kendall test (+ for increasing and − for decreasing). Magnitude of the trend is expressed by Sen's estimator of the slope of all the data points.

Table 1. Trends of rainfall in gauging stations in Syria

Station	Latitude	Longitude	Trend (X-V)
Idlib	35°55´58´´	36°38´30´´	-0,04338
Armanaz	36°05´09´´	36°30´14´´	-0,03931
Arihah	35°48´50´´	36°36´27´´	-0,08397
Addana	36°13´07´´	36°46´06´´	0
Maarrat Misrin	36°00´46´´	36°40´17´´	-0,06
Ebla	35°56´08´´	36°37´23´´	-0,08397
Haram	36°12´44´´	36°31´12´´	-0,04116
Khan Shaykhun	35°26´31´´	36°39´26´´	-0,04958
Darkush	35°59´30´´	36°23´37´´	0,013492
Saraqib	35°51´43´´	36°47´52´´	-0,04265
Kafar Takharim	36°07´06´´	36°30´58´´	-0,01029
Kafr Nabl	35°36´51´´	36°33´39´´	-0,05313
Moh. Wadi Eldaif	35°64´42´´	36°70´20´´	-0,06618
Tell Beydar	36°44´19´´	40°35´11´´	-0,06618
Tell 3alo Althanya	36°56´19´´	41°47´16´´	-0,06618
Al Qunaytirah	33°07´14´´	35°49´31´´	-0,06923
Hader	33°16´56´´	35°49´50´´	-0,08333
Nada Alsakher	33°05´11´´	35°56´32´´	-0,04845
Azaz	36°35´13´´	37°02´52´´	-0,06597
Al Bab	36°22´21´´	37°30´57´´	-0,02727
Al Safira	36°05´03´´	37°22´18´´	-0,056
Jarabulus	36°49´08´´	38°00´27´´	-0,03404
Aleppo Int. Airport	36°10´50´´	37°13´27´´	-0,00638
Kobani	36°53´26´´	38°20´59´´	-0,04583
Aleppo	36°12´14´´	37°08´02´´	0,057377
Afrin	36°30´45´´	36°51´55´´	0,028261
Manbij	36°32´10´´	37°58´03´´	**-0,06604**
Al Rastan	34°55´32´´	36°44´00´´	0,017895
Al Quaryatayn	34°13´51´´	37°14´18´´	-0,00451
Al Qusayr	34°30´30´´	36°34´56´´	-0,01739

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Table 1. (continued)

Station	Latitude	Longitude	Trend (X-V)
Al Mukharram	34°46´19´´	37°33´02´´	-0,0125
Al Nasrah	34°47´30´´	36°17´24´´	0,006667
Palmyra	34°34´14´´	38°17´31´´	-0,00405
Taldou	34°52´24´´	36°31´40´´	-0,0125
Tal Kalakh	34°40´06´´	36°15´27´´	0,125316
Homs	34°44´05´´	36°42´46´´	0,002532
Shin	34°46´55´´	36°25´21´´	0,011702
Marmarita	34°46´49´´	36°15´36´´	-0,075
Izraa	32°50´43´´	36°13´30´´	0,001149
Shaikh Maskin	32°49´40´´	36°09´35´´	0
As Sanamayn	33°04´30´´	36°10´53´´	0
Al Musayrfah	32°37´58´´	36°20´00´´	0
Tal Shihab	32°41´21´´	35°59´09´´	0,002564
Daraa	32°37´36´´	36°06´11´´	0
Nawa	32°53´14´´	36°02´25´´	-0,00417
Al Tal	33°36´33´´	36°19´02´´	-0,02429
Al Qutayfah	33°44´22´´	36°35´45´´	-0,02128
Al Kiswah	33°21´32´´	36°15´08´´	-0,00769
Al Nabk	34°00´49´´	36°44´00´´	**-0,04615**
Duma	33°34´23´´	36°24´33´´	-0,01696
Al Zabadani	33°43´34´´	36°06´14´´	-0,068
Umuyyad Mosque	33°30´41´´	36°18´23´´	0
Serghaya	33°48´40´´	36°09´25´´	-0,05862
Qatana	33°26´23´´	36°05´02´´	-0,04348
Maysaloon	33°30´59´´	36°17´22´´	-0,08
Yabrud	33°58´22´´	36°39´26´´	-0,02752
Abu Kamal	34°29´57´´	40°28´10´´	-0,00435
Al Busayrah	35°09´17´´	40°25´43´´	-0,01964
Al Tebni	35°36´17´´	39°49´09´´	-0,00562
Al Mayadin	35°00´59´´	40°26´47´´	-0,00625
Deir ez-Zur	35°19´50´´	40°08´04´´	-0,0063
Ash Shaykh Badr	34°59´26´´	36°04´52´´	-0,05741
As Sifsafeh	34°43´58´´	36°02´54´´	-0,12605
Al Qadmus	35°06´03´´	36°09´40´´	-0,11765
Baniyas	35°11´08´´	35°57´11´´	-0,01277
Draykish	34°53´44´´	36°08´07´´	-0,13019
Safita	34°49´09´´	36°07´08´´	-0,03333
Tartus	34°53´49´´	35°53´11´´	-8,7E-17
Mashta Al Hilu	34°52´42´´	36°15´17´´	-0,13793
Ar Reqqah	35°57´36´´	38°59´52´´	**-0,04962**
Tell Abiad	36°41´32´´	38°57´03´´	**-0,07294**
Ain Issa	36°23´03´´	38°52´03´´	**-0,05556**
As Suwayda	32°42´49´´	36°33´58´´	-0,0413
Shahba	32°51´26´´	36°37´31´´	-0,04237
Salkhad	32°29´09´´	36°42´42´´	-0,03636

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Regarding trend analysis of monthly rainfall data (Table 1.) is proved clear decreasing trend in rainfall over all Syria. Statistically significant negative trends are identified in climatic station Manbij, Al Nabk, Ar Reqqah, Tell Abiad, Ain Issa (Table 1.). It means the decreasing of rainfall in almost all gauging stations in the country, especially north (mountainous) and western (coastline) parts of the country. The trend slope decrease of rainfall is up 0.07 mm/year.

4. CONCLUSIONS

The study of the evaluation of rainfall time series by statistical methods is performed with goal to reduce impacts of extreme hydrological events – floods and droughts. Droughts is the most complex but least understood of all natural hazards. It is broadly defined as “severe water shortage”. Floods cause huge mainly material damages. Mentioned natural hazards cause loss of life, human and animal suffering and damage to economy and environment. The present study area is prone to extreme climate events such as drought and flood. The objective of this study was to investigate rainfall trends in chosen gauging stations in Syria. Annual rainfall trends were detected by Mann-Kendall statistical test. Negative trends of annual rainfall were found in the analyzed rainfall gauging stations, especially in thy western part of the country. In conclusion, Syria has shown decreasing trend of annual rainfall. It proved previous IPCC studies.

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References

[1] IPCC Working Group II: *Impacts, Adaptation and Vulnerability. Extreme high temperature and precipitation events*. http://www.ipcc.ch/ipccreports/tar/wg2/index.php?idp=625

[2] Sayemuzzaman, M., Jha, M.K. 2014. Seasonal and annual precipitation time series trend analysis in North Carolina, United States. *Atmospheric Research*, **137**, 183-194.

[3] Zeleňáková, M., Purcz, P., Gargar, I.A.K, Hlavatá, H. 2013. Comparison of precipitation trends in Libya and Slovakia. In: *River Basin Management 7*. Southampton: WIT Press, p. 365-374.

[4] Houghton, J.T., et al. 1996. *Climate Change 1995: The Science of Climate Change*. Working Group I, Second Assessment Reportof the Intergovernmental Panel on Climate Change (IPCC). Cambridge University Press, UK.

[5] Xu, Z.X., Takeuchi, K., Ishidaira, H., Li, J.Y., 2005. Long-term trend analysis for precipitation in Asia Pacific Friend river basin. *Hydrological Processes*, **19**, 3517-3532.

[6] Endo, N., Matsumoto, J., Lwin, T. 2009. Trends in precipitation extremes over Southeast Asia. *SOLA 5*, 168–171. http://dx.doi.org/10.2151/sola.2009-043.

[7] Almazroui, M., Islam, N.M., Jones P.D., Athar, H., Rahman, A.M. 2012. Recent climate change in the Arabian Peninsula: Seasonal rainfall and temperature climatology of Saudi Arabia for 1979–2009. *Atmospheric Research*, **111**, 29-45

[8] Almazroui, M., 2011. Calibration of TRMM rainfall climatology over Saudi Arabia during 1998–2009. *Atmospheric Research*, **99**, 400–414. doi:10.1016/ j.atmosres.2010.11.006.

[9] Ragab, R., Prudhomme, C., 2000. Climate change and water resources management in the southern Mediterranean and Middle East countries. *The Second World Water Forum*, 17-22.

[10] Modarres, R., Silva, V.P.R. 2007. Rainfall trends in arid and semi-arid regions of Iran. *Journal of Arid Environments*, **70**, 344-355.

[11] Tabari, H., Talaee, P.H. 2011. Temporal variability of precipitation over Iran: 1966-2005. *Journal of Hydrology*, **396**, 313-320.

[12] Nations Online. 2016. *One World.* The Nations Online Project: Get In Touch with the World http://www.nationsonline.org/oneworld/map/syria-map.htm

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C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
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[13] Climate Change Knowledge Portal. 2016. *Average monthly temperature and rainfall for Syrian Arab Republic from 1900-2012*. http://sdwebx.worldbank.org/climateportal/index.cfm?page=country_ historical_ climate &ThisRegion=Middle%20East&ThisCcode=SYR
[14] Kendall, M.G. 1975. *Rank Correlation Measures*. Charles Griffin, London.
[15] Mann, H.B. 1945. Non-parametric tests against trend. *Econometrica*, **13**, 245-259.
[16] Burn, D.H., Hag Elnur M.A. 2002. Detection of hydrologic trends and variability. *Journal of Hydrology*, **255**, 107-122.
[17] Partal, T., Kahya, E. 2006. Trend analysis in Turkish precipitation data. *Hydrological Processes*, **20**, 2011-2026.
[18] Yue, S., Hashino, M. 2003. Temperature trends in Japan: 1900–1990. *Theoretical and Applied Climatology*, **75**, 15-27, 2003.
[19] Sen, P.K. 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistical Association*, **63**, 1379-1389.
[20] Jain, S.K., Kumar, V., Sahariad, M. 2012. Analysis of rainfall and temperature trends in northeast India. *Intetnational Journal of Climatology*. Published online in Wiley Online Library. doi: 10.1002/joc.3483

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XIII

Comparative life cycle assessment of three water intensive tree cropping systems

K. Komnitsas[1*], G. Bartzas[2], D. Zaharaki[1], D. Vamvuka[1]

[1] School of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Greece
[2] School of Mining and Metallurgical Engineering, National Technical University of Athens, 15780 Athens, Greece
*Corresponding author: Email: komni@mred.tuc.gr

Abstract

A comparative life cycle assessment (LCA), through the use of GaBi 6 software package and specific related databases, of three water-intensive cropping systems was conducted in order to evaluate energy consumption and environmental impacts based on semi-intensive cultivation conditions. Results are provided for three fruit and nut tree crops traditionally cultivated in two representative areas in Greece, namely apples and almonds (Agia, East Thessaly region) and pistachios (Aegina Island, Attica region). In this context, detailed life cycle directories were created in an attempt to carry out a cradle to farm gate analysis by taking into consideration energy-related processes that are often excluded from agricultural LCA studies, such as machinery manufacture, nursery production and raw materials transportation. The impact categories considered include global warming potential (GWP), eutrophication potential (EP), acidification potential (AP) and cumulative energy demand (CED). According to the results of this study, apples present the best environmental profile while the other two cropping systems, almonds and pistachios, showed limited differences between them for all the impact categories evaluated. The phases of irrigation system and nutrient management were identified as the main “hot-spots” with the highest environmental impact and energy consumption in all crops under assessment and thus improvements to reduce those impacts were proposed.

Keywords: LCA; apples; almonds; pistachios; water-intensive crops

1. INTRODUCTION

Irrigated agriculture constitutes by far the largest consumer of freshwater at global scale and produces around 40% of global food supply [1]. Particularly in the semi-arid and arid regions of Southern Europe, the majority of scarce freshwater resources allocated to agricultural use accounting for up to 80% of the total withdrawal, often lead to total abstraction rates that exceed long-term natural rates of groundwater replenishment. At country level, the irrigated area has doubled over the last forty five years and now represents 37% of the total cultivated agricultural land [2]. As a result, 3,763 cubic metres of water were used per hectare of irrigated land in 2010, implying great energy consumption for withdrawal, transport and water application to crops and thus increase in associated greenhouse gas (GHG) emissions.

As an efficient methodology to evaluate and compare the potential effects of all the inputs and outputs throughout the whole life cycle of a product on the environment, Life Cycle Assessment (LCA) has been widely applied to assess the environmental impacts of many agricultural products including consumptive water for irrigation [3]. However, most previous LCA studies for crops grown at farm scale only provide information for the related environmental impacts from the cultivation of fruit trees and only very few refer to nut trees, such as almonds and pistachios [4,5].

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These studies have shown that the cultivation of both nuts could be improved in terms of growth and yield, crop quality and orchard longevity contrary to those traditionally cultivated under rain-fed/drought conditions [6]. In fact, recent studies have shown that both almonds and pistachios are considered among the most water-intensive crops when irrigation is applied [7]. To this context, this LCA study attempts to (i) analyze and compare the life cycle of three typical water-intensive tree cropping systems cultivated in Greece; namely, apples, almonds and pistachios, (ii) identify critical processes that are energy intensive and cause most environmental impacts, and (iii) provide suggestions for improving the environmental performance of the cultivation systems under study. Special emphasis was given to the cultivation practices (irrigation and fertilization) used for the production of pistachios in the semi-arid island of Aegina in relation to those utilized for fruit and nut trees in more humid and rainy agricultural regions of the mainland Greece.

2. MATERIALS AND METHODS

2.1 Study areas

Two study areas representative of the main production regions for apples, almonds and pistachios in Greece were selected, namely (i) Agia, located in the prefecture of Larissa, region of Thessaly, and (ii) Aegina Island, located in the prefecture of Piraeus, region of Attica, as shown in Fig. 1.

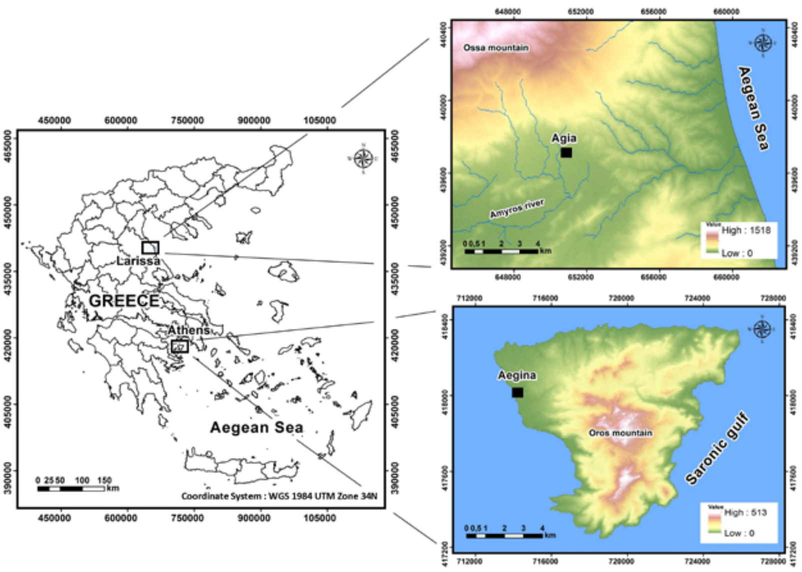


Figure 1. **Study areas**

Agia is located about 35 km east of the capital town of the region, Larissa, and 12 km from the Aegean coast. It has a population of 3,169 inhabitants, while its total valley area is 63 km^2, of which 75% is arable. The climate in the study area is typical Mediterranean, with mean summer temperature ranging between 16.5 and 20.4 °C, and mean winter temperature remaining almost stable (~6 ^oC) [8]. The mean annual temperature in the study area over the last 4 year period (2012–2015) was 15.4 °C and the average annual precipitation was 638 mm, mostly concentrated in autumn. The topographic relief is semi-mountainous and reaches up to 1518 m above the sea level (a.s.l) in the north western part of the study area (Ossa mountain). On the other hand, the island of Aegina is characterized by semi-arid Mediterranean climate, with a mean annual temperature of 19 °C and an annual rainfall of 295 mm, of which almost 80% is recorded in the wet period (November-April), while summers are usually dry.

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Agia is among the leading producer areas in Greece with 18 and 20% of the total annual production of almonds and apples respectively, while 11% of the total pistachio production of the country is recorded in Aegina [9,10]. However, the study area of Aegina is world known for its ideal climate conditions and unique soil composition that yields/promotes the production of high quality Protected Designation of Origin (PDO) pistachios with premium pricing in the EU market, due to their particular organoleptic characteristics, excellent flavor and appeal. Table 1 presents the main agronomic data for the semi-intensive production of apples and almonds in Agia as well as PDO pistachios in Aegina.

Table 1. Main agronomic characteristics of the three semi-intensive cropping systems

Characteristics	**Unit***	**Orchards**		
		Apples	**Almonds**	**Pistachios**
Cultivar	-	Granny Smith	Texas	Aegina
Orchard age	years	25	30	40
Density	trees ha^{-1}	850	300	250
Yield**	t ha^{-1}	32.4	3.3	2.5
Harvest period	-	3rd week of October	3rd week of September	1st week of September
Irrigation technique	-	drip irrigation and micro-sprinklers	double drip irrigation	furrow and drip irrigation
Irrigation period	-	June to October	April to September	April to September
Fertilizers rate				
N	kg ha^{-1}	80	180	230
P (as P_2O_5)	kg ha^{-1}	90	100	90
K (as K_2O)	kg ha^{-1}	180	200	200
Pesticides rate	kg ha^{-1}	46	8.2	5.4
Irrigation water	m^3 ha^{-1}	3,400	4,650	4,450

*Mean values are given for the period 2011-2015; ** refer to FU (functional unit) production

2.2 LCA methodology

The LCA methodology adopted in this study was applied according to the principles and specific requirements of the International Organization for Standardization (ISO) 14040-14044 standard series [11,12]. Therefore, in this study, the functional unit selected was the marketable production of 1 tonne of fresh apples, nutmeat (kernel) almonds and in-shell pistachios. This functional unit was set as reference/ basis to assess, and in particular compare the varying input and output flows of the different cropping systems considered. Since the purpose of this study was to compare the three systems on a common basis, it was deemed appropriate not to follow any allocation approach. Therefore, co-product credits were not estimated.

LCA modelling was performed with the software package Gabi 6.0 using the characterization factors of the well-established CML Baseline 2001 method [13] supplemented with the cumulative energy demand (CED) [14]. As a result, the indicators of four environmental impact categories were estimated: global warming potential for 100 years (GWP), eutrophication potential (EP), acidification potential (AP) as well as cumulative energy demand (CED), as an energy flow

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indicator. The system boundaries used in this study considered all the production processes involved, from raw materials extraction (i.e the cradle) until post-harvesting of the cropping systems (i.e the farm gate). Based on the system boundaries, foreground and background processes/flows were structured in six common and stand-alone phases to facilitate data compilation and comparative assessment. The phases included were irrigation system, fertilizers production, pesticides production, agricultural machinery (production and maintenance), field management employing farm level operations such as agrochemical application, land preparation/ploughing, tillage, pruning and harvest as well as post-harvest (drying, shelling and hulling) along with waste management. For the transportation of raw materials (fertilizers and pesticides), road transport by truck/lorry and the associated fuel consumption were considered in each phase tracked.

Life cycle inventory (LCI) for the three cropping systems was built based on primary data collected from 28 semi-intensive orchards with full productive mature trees and by considering a 6-month seasonal period of irrigated agricultural activities. For this, a questionnaire has been prepared and personal interviews with experts and farmers were performed. As a result, all relevant inputs and outputs related to crop production and their associated indirect/direct emissions were identified and quantified. To support reliability and representability, survey data were compiled into average-weighted inputs for operations and outputs in each area studied. Background data were retrieved from national and EU databases, literature as well as the available LCI databases (Professional and Ecoinvent v.3.1) of the software used.

3. RESULTS AND DISCUSSION

3.1 Cumulative impacts per tree cropping system

The absolute values of each impact category and the cumulative energy demand for the three studied cropping systems are presented in Table 2. For example, the production of 1 tonne of pistachios in Aegina has an overall impact of 8.71 kg SO_2-eq for AP, 3.84 kg PO_4-eq for EP, 2,119 kg CO_2-eq for GWP and 28.05 GJ for CED.

Table 2. Environmental impact categories of the three tree cropping systems under analysis

Impact category	Acronym	Apples	Almonds	Pistachios
Acidification potential (kg SO_2-eq. FU^{-1})	AP	0.95	8.24	8.71
Eutrophication potential (kg PO_4-eq. FU^{-1})	EP	0.44	3.62	3.84
Global warming potential (100 years) (kg CO_2-eq. FU^{-1})	GWP	109	2,009	2,119
Cumulative energy demand (GJ FU^{-1})	CED	0.96	27.33	28.05

FU: functional unit (1 tonne of fresh apples, nutmeat (kernel) almonds and in-shell pistachios)

In general, the results show that the cultivation of apple tress has the lowest impacts for all impact categories, whereas impacts were found to be higher but almost similar for almond and pistachio production. The primary energy consumption was 0.96 MJ kg^{-1} for apples, 27.33 MJ kg^{-1} for almonds and 28.05 MJ kg^{-1} for pistachios. As a result, apples exhibited significantly lower value for GWP than almonds and pistachios (109 kg CO_2-eq. per tonne produced vs 2,009 and 2,119 kg CO_2-eq., respectively). This was largely because lowest yields are obtained for almonds and pistachios (3.3 and 2.5 t ha^{-1}, respectively), compared to fresh apples (32.4 t ha^{-1}). With regard to acidification and eutrophication potentials, the main differences were due to the lower dose of N-containing fertilizers applied in the apple orchards (80 kg ha^{-1} vs. 180-230 kg ha^{-1} for almonds and

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pistachios) and subsequently the lower associated emissions, mainly as nitrous oxides, from related raw materials extraction and manufacture industry. Specifically, AP of the studied life cycles varied from 0.95 kg SO_2-eq for apples to almost 9 times higher for almonds and pistachios. Regarding EP, the lowest value calculated in this study was 0.44 kg PO_4-eq. for the apple cropping system, followed by the almond (8.24 PO_4-eq.) and pistachio (8.71 PO_4-eq.) cropping systems.

On the other hand, although almond orchards had a slightly lower total environmental impact compared to pistachio orchards, the differences in impacts between these two nut cropping systems were minor (5-6%), while for CED the difference was almost negligible (2%). This is due to the similarities in orchard management practices used in both nut tree cropping systems and to some extent, balances among inputs of raw materials (N/P/K fertilizers, pesticides and irrigation water).

3.2 Contribution analysis

In order to elucidate the origin of environmental and energy burdens and associate them with specific LCI phases in order to identify the main "hot spots", a contribution analysis was carried out. Figure 2 shows the comparative contribution of each productive phase, expressed in % for each impact category studied, for the three water-intensive tree cropping systems under assessment.

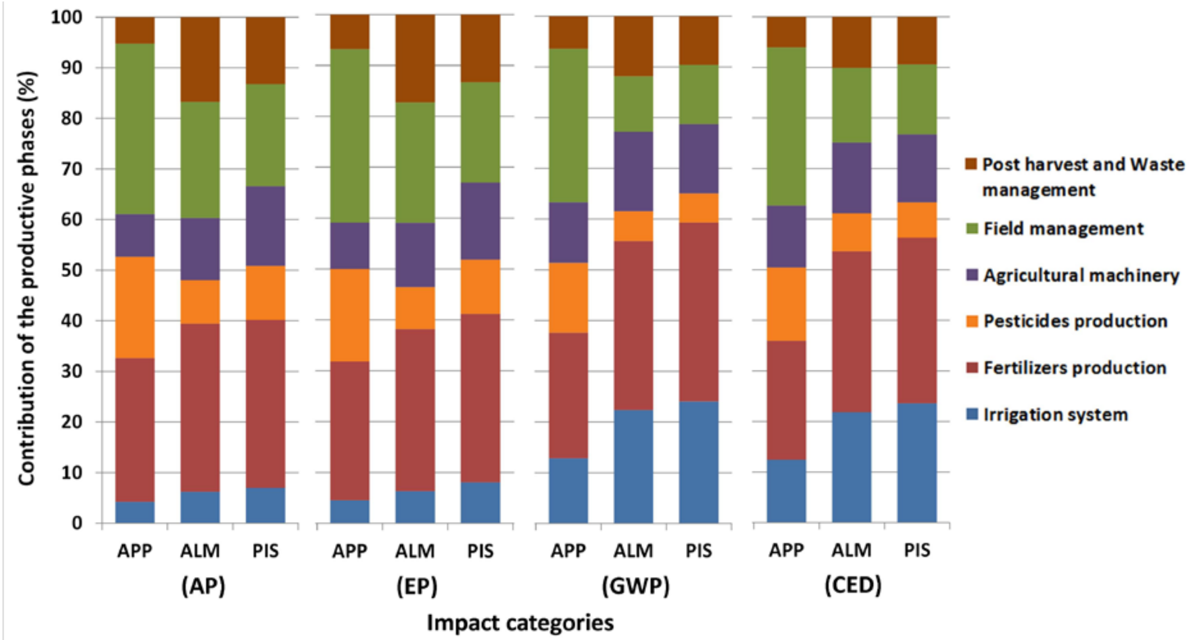


Figure 2. Comparative contribution of each productive phase to each impact category for the three water-intensive tree cropping systems under assessment (APP: apples; ALM: almonds; PIS: pistachios) (AP: acidification potential; EP: eutrophication potential; GWP: global warming potential and CED: cumulative energy demand).

In general, for apple tree cultivation the highest contribution to all impact categories originated from field management, which contributed 30-34% to the cumulative impact, mostly due to high dose of pesticides applied (46 kg ha^{-1}) and the contribution of its related on-field air, soil and water emissions. On the other hand, for almonds and pistachios orchards fertilizers production had the highest contribution to all impact categories, varying between 31-33% and 33-35%, respectively. This was heavily influenced by the substantial fertilizer requirements of almond and pistachio production in both cultivation regions, due to emissions derived from raw material (ammonium nitrate and sulfate, potassium chloride, single superphosphate, fossil fuels) extraction and processing during their life cycle.

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More in detail, fertilizers production was responsible for approximately 33% of the estimated cumulative impacts for AP in both nut tree cropping systems. This was attributed primarily to the NH_3 and NO_x emissions caused during production, as well as SO_2 emissions derived from fossil fuel combustion during transportation of raw materials to tree orchards. The second highest contributor to impact category of AP was the field management phase, which accounted for 23% and 20% in the almond and pistachio cropping systems, respectively. In the case of apple production, field management was the most impactful phase, responsible for 34% of the cumulative impacts, mainly due to the use of considerable amounts of agrochemicals. Production of fertilizers represented also a significant burden for the AP impact category, contributing 28% in the cumulative impacts, followed by the pesticides production phase (20%).

As for the previous impact category, field management represented the highest burden with regard to EP in the apple orchards, contributing 34% in the cumulative impacts, followed by the phases of fertilizers production (27%) and pesticide production (18%) as a result of raw materials extraction and related manufacture. In almond and pistachio orchards, EP was dominated by emissions originated from the production of chemical fertilizers, accounting for about 32% of the total cumulative impacts for both nut tree cropping systems. In relation to GWP, contribution analysis showed that field management was the most impactful phase with regard to apple production, accounting for 30% of the cumulative impact. Similarly to AP and EP impact categories, fertilizers production and irrigation system allocated the highest share of the GWP in the almond and pistachio orchards, due to the big quantities of fossil fuels required for manufacture /production operations and pumping groundwater, respectively.

Regarding CED, field management accounted for 31% of the total energy inputs in apple orchards, followed by fertilizers production (24%) and pesticides production (14%). Conversely, the most energy consuming phase in both nut tree cropping systems studied was fertilizers production, which contributed 32% and 33% to the total energy inputs estimated in almond and pistachio orchards, respectively. Significant energetic impacts were calculated in terms of CED for the irrigation phase (22% and 24% for almonds and pistachios, respectively), due to electricity consumption for pumping groundwater and fossil fuels requirements for the manufacture and processing of the elements needed for the production of the irrigation system, namely steel for pumps and injectors, polyethylene for pipes and polyvinyl chloride for electro-valves [3].

All other phases included in the LCA had lower contributions to the impact categories assessed. Averaged across impact categories, the machinery production phase was responsible for approximately 12% of cumulative impacts in all three semi-intensive tree cropping systems. This was mainly due to the fossil fuel requirements for their manufacture/production, transport of raw materials and their associated combustion emissions, as well as due to maintenance activities from the end-of-life management of used equipment and other materials. As expected, almond and pistachio cultivation, contrary to apples, is characterized by the highest contribution of post harvest and waste management activities to all impact categories. Hulling/shelling operations, as well as other on-farm activities, including also auxiliary operations such as drying, pre-cleaning, sorting, grading and dust removal, cause considerable GHG emissions (up to 17% for almonds in AP and EP impact categories) during the peak period (September), as their demand for electricity is high. However, around 60% of the GHG emissions of this phase were associated with the generation of considerable waste volumes during post harvesting activities, since in most cases waste hulls and shells are left in an exposed/uncontrolled site or even buried at the farm site.

3.3 Hot spots and suggestions

Based on the results of the contribution analysis, the phases of fertilizers production, irrigation system and field operations were identified as “hot spots”, since their impact contributions were found to be remarkably high in all tree cropping systems studied. More specifically, the contribution of the fertilizers production to impacts was considerably high, varying from 23% for CED in the

apple orchards to 35% for GWP in the pistachio orchards. Reduction of the environmental footprint of this phase can be accomplished by enhancing energy efficiency in the production facility or by reducing the associated emissions with the use of de-N_2O catalyst systems, minimizing the transport distance between production areas and cultivation sites and adjusting the application rate of fertilizers to the related N/P/K demand for each tree cropping system studied. A shift in the existing nutrient management from energy-intensive chemical to eco-friendly organic fertilizers (manure, compost) or their combined application may drastically reduce emissions by 30% and energy use by half. In this context, composting/reuse of available bio-waste and crop residues (prunings, hulls and shells) at an orchard level can be a useful and low-cost measure to improve sustainability of agricultural production [3,15] as well as minimize extensive use of chemical fertilizers at field-level, especially the high nitrogen demand of pistachios in comparison to two other crops studied.

The irrigation system was another important energy-driven and GHG-intensive phase identified via contribution analysis for the two nut tree cropping systems studied. This phase is of paramount importance in Aegina, where limited water resources are available, thus intense over-pumping of the shallow aquifers is required during the dry summer period when irrigation requirements for pistachios are maximum. Based on the results obtained in this study, the highest impacts from irrigation reached 22% and 24% of the cumulative impact for GWP in the almonds and pistachios orchards, respectively, mainly due to the higher amounts of water pumped for irrigation (4,450 and 4,250 m^3 ha^{-1}) compared to apple orchards (3,400 m^3 ha^{-1}). It is important to note here that even though the amount of water used in the present study for the production of pistachios is significantly low compared to California with 10,000 m^3 ha^{-1} [16] and Cyprus with 7500 m^3 ha^{-1} [17], the energy consumption for pumping groundwater is higher since the aquifer in Aegina is characterized by increased salinity . Therefore, reduction of the cumulative impact associated with irrigation, can be achieved by (i) increasing water irrigation efficiency with the use of micro-irrigation systems (mini- and micro-sprinklers) that can achieve water savings up to 40% per m^2 compared to conventional irrigation techniques (furrow/surface flooding), (ii) regular maintenance of the pumping units and their components (pipes, electro-valves) to prevent efficiency loss due to clogging and corrosion damage due to saline water used, (iii) monitoring the irrigation water quality on a frequent basis in order to select the appropriate screen and media filter, and (iv) using a targeted irrigation scheduling program (rates and timing) to maintain the best possible soil-water relationship for optimal tree yield.

The results of the contribution analysis identified the phase of field management as the most impactful phase in the life cycle of apple production (30-34% to all impact categories) and also clearly indicated its significant contribution (11-24%) in the life cycle of almonds and pistachios, especially for the impact categories AP and EP. It is important to note that the control of insects and weeds in apple tree cropping systems is necessary for the production of a high-quality marketable product, compared to nut tree cropping systems that are more tolerant to natural diseases. Therefore, in the case of apple production, potential mitigation of greenhouse gas emissions can be achieved by minimizing pesticide application rates through the use of crop sanitation, application of spot-treatment equipment to improve pest efficiency, installation of protective netting and adoption of cross-protection techniques. Other possible strategies to achieve reduction of emissions in all studied cropping systems related to farm management phase may include proper sizing and use of more energy efficient machinery, rational application of agrochemicals to match requirements for each crop and use of alternative cultivation practices such as conservation tillage and pruning. However, since in practice field cropping operations depend strongly on site-specific conditions such as soil quality, climate and orchard level conditions, use of monitoring techniques (e.g. soil and leaf tissue sampling and analysis) at frequent intervals for the determination of the main agronomic characteristics is of great importance.

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4. CONCLUSIONS

Considering the difficulties in performing a comparative LCA study between different tree cropping systems exhibiting variability in terms of yield, cultivation practices, post-harvest operations, waste management, and other site-specific conditions such as climate, irrigation water availability and quality, this study examined the life cycle of apple, almond and pistachio production in two representative areas in Greece. The LCA methodology has been successfully applied in order to identify the activities causing the highest impacts across and within the studied life cycle and provide guidelines for potential improvements in order to reduce environmental impacts.

Given the fact that dissimilarities between tree cropping systems are unavoidable, apple orchards exhibited the best overall environmental performance, with lower GHG contributions in all production phases compared to the other two cropping systems studied (almonds and pistachios). On the other hand, the LCA indicated that the two nut tree cropping systems performed quite similarly with respect to all impact categories as result of their relatively similar agronomic characteristics.

The results of the contribution analysis showed that the phases of fertilizers production, irrigation system and field management were responsible for the largest share of energy consumption and the associated GHG emissions in the three water-intensive tree cropping systems. It is important to note that this study considered the cultivation of species that are common in Greece, but its results can be easily applied in similar arid and semi-arid environments, not only in the Mediterranean region but also elsewhere. Finally, further studies, including scenario analysis, are needed to analyze possible alternative future developments in a tree product chain and quantify them in terms of energy conservation, emissions reduction and agricultural sustainability.

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References

[1] Peña-Arancibia, J.L., Mainuddin, M., Kirby, J.M., Chiew, F.H.S. McVicar, T.R. Vaze, J., (2016). Assessing irrigated agriculture's surface water and groundwater consumption by combining satellite remote sensing and hydrologic modelling. *Science of the Total Environment*, **542(A)**, 372 – 382.

[2] Eurostat, 2010. http://ec.europa.eu/eurostat/statistics-explained/index.php/Agricultural_census_ in_ Greece (accessed December 10, 2015).

[3] Bartzas, G., Zaharaki, D., Komnitsas, K., 2015. Life cycle assessment of open field and greenhouse cultivation of lettuce and barley. *Information Processing in Agriculture*, **2(3–4)**, 191 – 207.

[4] Marvinney, E., Kendall, A., Brodt, S., 2014. A comparative assessment of greenhouse gas emissions in California almond, pistachio, and walnut production. *Proceedings of the 9th International Conference on Life Cycle Assessment in the Agri-Food Sector (LCA Food 2014)* (eds R. Schenck and D. Huizen), October 8-10, San Francisco, California, USA, 761–771.

[5] Volpe, R., Messineo, S., Volpe, M., Messineo, A., 2015. Carbon Footprint of Tree Nuts Based Consumer Products. *Sustainability*, ***7*(11)**, 14917 – 14934.

[6] Memmi, H. Gijón, M.C., Couceiro, J.F., Pérez-López, D. 2016. Water stress thresholds for regulated deficit irrigation in pistachio trees: Rootstock influence and effects on yield quality. *Agricultural Water Management*, **164(1)**, 58 – 72.

[7] Medellín-Azuara, J., Howitt, R.E., Harou, J.J., 2012. Predicting farmer responses to water pricing, rationing and subsidies assuming profit maximizing investment in irrigation technology. *Agricultural Water Management,* **108**, 73 – 82.

[8] NOA (National Observatory of Athens) network, 2015. http://stratus.meteo.noa.gr/front (accessed November 10, 2015).

[9] HSA (Hellenic Statistical Authority), 2012. http://www.statistics.gr/en/statistics/-/publication/ SPG06/2012 (accessed December 10, 2015).

ISBN: 978-960-6865-94-7

[10] FAO (Food and Agriculture Organization of the United Nations), 2013. FAOSTAT. http://faostat3.fao.org/home/E. (accessed December 10, 2015).
[11] ISO, 2006a. Environmental Management – Life Cycle Assessment – Principles and Framework, ISO 14040. ISO, Geneva, Switzerland.
[12] ISO, 2006b. Environmental Management – Life Cycle Assessment – Requirements and Guidelines, ISO 14044. ISO, Geneva, Switzerland
[13] Guinée, J.B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn R., Koning A.D., Oers, L.V., Wegener Sleeswijk, A., Suh, S., Udo de Haes, H.A., Bruijn, H.D., Duin R.V., Huijbregts M.A.J., 2002. *Handbook on Life Cycle Assessment. Operational Guide to the ISO Standards*, Kluwer Academic Publishers, Dordrecht (the Netherlands).
[14] Hischier, R., Weidema, B., Althaus, H.J., Bauer, C., Doka, G., Dones, R., Frischknecht, R., Hellweg, S., Humbert, S., Jungbluth, N., Köllner, T., Loerincik, Y., Margni, M., Nemecek, T., 2010. *Implementation of Life Cycle Impact Assessment Methods*, ecoinvent Report No. 3 (version 2.2), Dübendorf, Switzerland: Swiss Centre for Life Cycle Inventories.
[15] Komnitsas, K., Zaharaki, D., Pyliotis, I., Vamvuka, D., Bartzas, G., 2015. Assessment of pistachio shell biochar quality and its potential for adsorption of heavy metals. *Waste and Biomass Valorization,* **6,** 805 - 816.
[16] Johnson., R., Cody, B.A., 2015. *California Agricultural Production and Irrigated Water Use, Congressional Research Service Report No. R44093*, available at: https://www.fas.org/sgp/crs /misc/R44093.pdf (accessed December 18, 2015).
[17] Gregoriou, C., 2001. *Collection, conservation and utilization of Pistacia genetic resources in Cyprus*. – In: Padulosi, S., A. Hadj-Hassan (eds.). Project on Underutilized Mediterranean Species. Pistacia: towards a comprehensive documentation of distribution and use of its genetic diversity in Central & West Asia, North Africa and Mediterranean Europe. Report of the IPGRI Workshop, 14-17 December 1998, Irbid, Jordan, 41 – 44.

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Oil contamination damage and the marine biodiversity: Caspian Sea and Black Sea

N. Sivri[1*], H. Kurtuluş Özcan[1], F. Ahmadli[1], E. Başar[2]

[1] Department of Environmental Engineering, Istanbul University, Istanbul 34320, Turkey.
[2] Department of Maritime Transportation & Management Engineering, Karadeniz Technical University, Trabzon 61600, Turkey.
*Corresponding author: Email: sivrin@gmail.com

Abstract

Oil Industry is known to be a leading figure in industrial pollution. Like other types of industries, oil industry is damaging on both offshore and onshore ecosystem with its waste. Oil spills can cause a wide range of impacts in the marine environment and are often portrayed by the media as "environmental disasters" with dire consequences predicted for survival of marine flora and fauna. Accidental spills of the contaminants pose a very high level of threat for the marine ecosystem and coastline. The economic fish species are very sensitive to continued high fluxes of contamination as the both of Caspian Sea and Black Sea are closed basins. The spilled oil could contaminate not only shorelines of oceans and lakes but also some of rivers and streams and other ecologically sensitive habitats along the water's edge.

In this study, the environmental pollution problems caused by petroleum reaching water bodies by accidents or intentional events during extraction, transportation or refining processes has been conducted and possible effects were investigated on Black Sea and Caspian Sea. Petroleum contamination examples in Black Sea were researched with different scenarios and potential similar accidents' damage effect on biodiversity to Caspian Sea region has been estimated. Apart from the possible effects of such risks on endemic and economic species, the procedures towards reducing these effects have been discussed. Both of the Black Sea and Caspian Sea, which are among the most remarkable water basins in the world, are unique ecosystems including endangered species and also other endemic and economic species detected by International Union for Conservation of Nature (IUCN). At this study oil contamination examples in Caspian Sea and Black Sea were researched and damage to Caspian region has been estimated for the case study. The other purpose of this research is to identify damages to ecosystems by oil industry wastes, to investigate prior studies conducted on this matter and make an evaluation.

Keywords: oil spill; biodiversity; endemic species; Caspian Sea; Black Sea

1. INTRODUCTION

Petroleum industry is a leading figure in industrial pollution division. Like other types of industries, petroleum industry harms both offshore and onshore ecosystem with its waste [1]. Freshwater and marine shoreline areas are important public and ecological resources. However, their cleanliness and beauty, and the survival of the species that inhabit them, can be threatened by accidents that occur when oil is produced, stored, and transported.

Oil is sometimes spilled from vessels directly into waterways; spills from land-based facilities can flow into waters and foul shorelines [2]. These accidents affect both oceans and freshwater environments. Despite the best efforts of response teams to contain spilled oil, some of it may

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contaminate shorelines of oceans and lakes, banks of rivers and streams, and other ecologically sensitive habitats along the water's edge [3].

Oil pollution of the ocean comes from shipping activity and offshore oil production. Seabed activities on oil exploration and production constitute a relatively small part in the general amount of the pollution of marine environment. The principal cause of marine pollution with oil is shipping. Oil may impact an environment by one or more of the following mechanisms: Physical smothering with an impact on physiological functions; chemical toxicity giving rise to lethal or sub-lethal effects or causing impairment of cellular functions; ecological changes, primarily the loss of key organisms from a community and the takeover of habitats by opportunistic species; indirect effects, such as the loss of habitat or shelter and the consequent elimination of ecologically important species [2]. Oil spills affect not only the ocean space around them, but also open waters and the seabed, wetlands and corals. They also damage fisheries and coastal amenities. The caused damage is unpredictable and does not depend on the size of the oil spill. It depends rather on the proximity to the shoreline and vulnerability of the area [4].

In this study, environmental pollution problems caused by petroleum reaching water bodies by accidents or intentional events during extraction, transportation or refining processes has been conducted and possible effects were investigated on Black Sea and Caspian Sea example. Petroleum contamination examples in Black Sea were researched with different scenarios and potential similar accidents' damage effect on biodiversity to Caspian Sea region has been estimated. The purpose of this study is to identify damages to water bodies by petroleum industry wastes, to investigate prior studies conducted on this matter and make an evaluation.

2. STUDY AREA

The Caspian Sea is the largest enclosed inland body of water on Earth by area, which extends 1 200 km from north to south and contains more than 40% of the inland waters of the world, variously classed as the world's largest lake or a full-fledged sea [5]. The Caspian Sea is commonly divided into three basins: the northern, middle and southern (Figure 1). The northern basin occupies 27% of the surface area of the Caspian Sea but is shallow, averaging only 5 m in depth and as a consequence, retains only 0.6% of the total volume of the Sea. Progressing southward, the depth increases considerably.

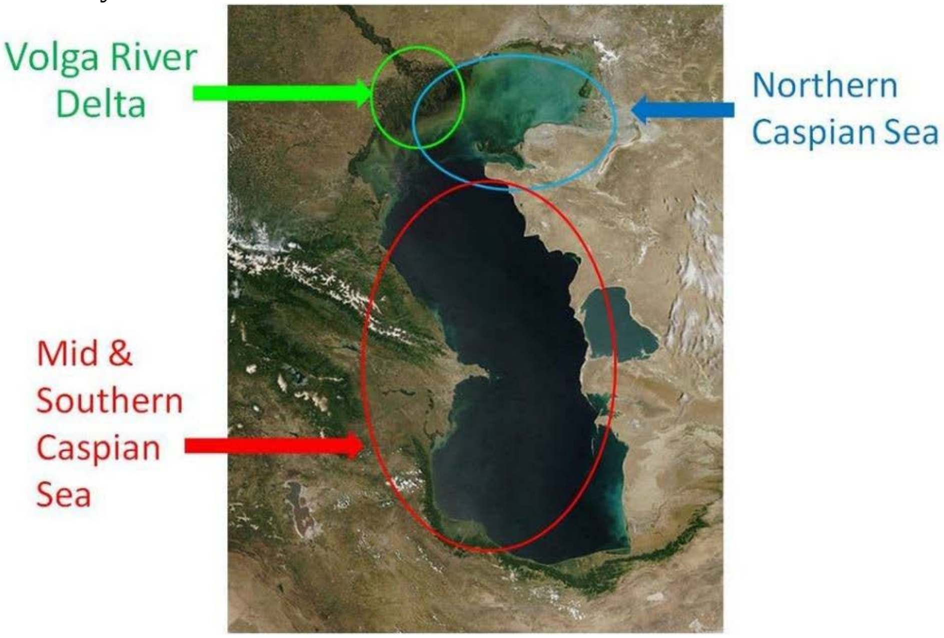


Figure 1: Basins of the Caspian Sea

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The Volga river delta is freshwater and home to freshwater algae, many species of waterfowl, and freshwater fish including carp, pike, and catfish [6] Marine species of fish and plankton generally dominate the central and southern portions of the Caspian where the salinity ranges from 10-14 [7]. These species include Caspian salmon, sturgeon, and herring [6]. Caspian salmon (actually a species of trout) and sturgeon also migrate up rivers such as the Volga and Ural for spawning [8].

Other significant sources of Caspian oil include onshore fields in Turkmenistan near the coast and production from Russia's North Caucasus region [9]. While most current Caspian oil comes from onshore fields, the biggest prospects for future growth in Caspian oil production will be from offshore fields, which are still relatively undeveloped. Caspian production accounts for virtually all oil production in some of the region's countries, including Azerbaijan and Turkmenistan, yet only a very small portion for the region's two largest producers, Russia and Iran. In total, production that can reasonably be classified as "Caspian oil" accounts for roughly 17 percent of the total production of the region's countries.

The biological diversity of the Caspian and its coastal zone makes the region one of the most valuable ecosystems in the world. Many species are endemic and there are many representatives from almost all major groups on earth. The numbers of species in the Caspian Sea are; *Phytoplankton* (449 species), *Zooplankton* (315 species), *Phytobenthos* (64 species), *Zoobenthos* (379 species), *Fishes* (126 species, 54 Endemic), *Mammals* (1 species, 1 Endemic), *Birds* (466 species) [8, 10, 11, 12, 13]. The longest established species are among the group of indigenous, brackish-water organisms. These include high percentage of endemic species and even genera[14]. The rest of the organisms found today are basically derived from the Mediterranean marine biogeographic region, the Arctic marine region or the freshwater (riverine) complex. Recent studies suggest the actual endemism may be even higher (Table 1). Almost all the indigenous species are found in the middle Caspian because of its relative stability over time, its salinity regime (consistently brackish) and its central location; consequently the highest number of endemic species is found there. However, the north Caspian has the greatest diversity of both habitats and species. This is due to the big rivers, such as the Volga and the Ural, which create a zone where marine and freshwater fauna are mixed. The Volga River system was also the ancient route for the penetration of Arctic and Mediterranean species which are still found in the Caspian. The existence of vast shallows, some deep depressions, the wide Volga Delta and other rivers, and fluctuations of salinity from 0.12 to 10 ‰ provide different ecological niches which, in turn, provide high species diversity [14].

Table 1: Endemic Species of Caspian Sea (adapted by Aubrey, 1994; Kasymov, 1994; Dumont, 1998; Dumont, 1999; Ivanov, 1997)

Natural marine resources	**Number of species**	**Natural marine resources**	**Number of species**
Spongia	4	Copepoda	23
Coelenterate	2	Isopoda	1
Turbellaria	29	Amphipoda	68
Nematoda	3	Cumacea	19
Rotatoria	2	Decapoda	1
Oligochaeta	2	Hydracarina	2
Cladocera	19	Mollusca	53
Ostracoda	3	Fishes	54
Mysidacea	20	Mammal	1

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The Caspian is characterised by a small variety of fish species compared to open ocean regions. Two of them are introduced foreigners: the flounders and a mullet (Mugilidae - family species), while another two - pipefish and a sand-smelt (Atherinidae - family species) originate from an unknown source. The most diverse are the families of goby, carp, herring and sturgeon. Local rare endangered species include: Caspian lamprey (*Caspiomyzon wagneri*), spiny sturgeon (*Acipenser nudiventris*), Volga herring (*Alosa kessleri volgensis*), Caspian salmon (*Salmo trutta caspius*), *Stenodus leucichthys*, *Chalcalburnus chalcoides chalcoides*, *Vimba vimba perca*, *Barbus brachycephalus caspicus*, *Barbus ciscaucasicus*, *Barbus capito*. Up to 126 subspecies may exist. Most are carps (33 %), gobies (28 %) and shads (14 %) [10,14].

The most important element of the fauna is the sturgeon, with 85 % of the world's population at its peak in the late 1970s. Different sturgeon species are the most valuable commercial fish in the Caspian. Important for their existence is the close proximity of brackish waters with rivers (the north Caspian being the most important example). Six species of sturgeon exist in the Caspian, belonging to the genera Huso and Acipenser. Kilka are a small, planktivorous, herring like fish native to the Caspian Sea. There are three commercially fished species of kilka in the Caspian Sea however several factors have resulted in the decline of this species. Kilka account for 80% of the total catch in the Caspian Sea [15].

2.1. Environmental Problems of the Black Sea and Caspian Sea Based on Oil

Environmental problems of the Black Sea and Caspian Sea are multiple and various in their origin. On one hand, they are caused by the commercial use of the sea; on the other hand, human activity impacts coastal areas, including input from rivers in the Caspian. Water pollution is caused by human activities along the coastal areas and near river systems, with additional water pollution originating from the seas. A growing proportion of water pollution involves oil exploitation, especially shelf-based, as well as construction and operation of marine platforms, gangways and underwater oil pipelines, refining and dredging. In addition, oil transport across the Black Sea and Caspian Sea contributes to water pollution through vessel leakage, ballast water discharge, pipeline leaks and, of course, all oil spills.

In oil spills, as soon as the oil contacts with the water, it tends to swim without being mixed with the water and to spread on the surface according to the physical specifications such as surface tension, viscosity, density etc. Owing to these characteristics, spread poses a vital threat for the organisms. Direct fatal toxic effect of oil products on sea organisms can be seen as the impact on accumulation and physiological activities in tissues and cells. Such contaminators affect eggs, larva and young members of living sources more. Sustainable generations of living sources and their chance to maintain their generations are under threat [16]. Physiological effects of contaminators can be ranged as following; causing delay and prevention for cell division in plankton; dietary changes in crustaceans; abnormal spawning and change in spawning periods in fish; and formation of cancerous tumors. The highest effect is observed in living communities, living in high tide-low tide line of the sea. Especially, photosynthetic plants, which play a significant role in sea ecosystem and provide oxygen for the water, are contaminated with the oil film spreading on the surface and they die [17].

3. METHOD

General Operational Modeling Environment (GNOME) developed by The National Oceanic and Atmospheric Administration (NOAA) is used to simulate spatial and temporal distribution of oil [18]. This software uses wind, tide, and current values to calculate the movement of oil at sea surface [19,20,21]. The simulation code GNOME version 1.3.9 is utilized to generate the oil spill scenarios.

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4. RESULTS & DISCUSSION

In recent years, many studies have been conducted through the results of the accidents or by the support of scenarios in order to prevent accidents related to oil exploration and drilling operations [22,23,24,25]. Nowadays, a special agency affiliated to the United Nations called International Maritime Organization (IMO) and Flag States, which are known as maritime industry regulators, require a pro-active assessment on new maritime technologies related to how they affect human safety and the environment before they give approval. In general, a risk analysis is used in order to conduct such assessment [26].

In the analysis on the results of the scenarios, the completion period for scenarios (NW, 5 knot) was observed as 10 days. At the end of the study, in these scenarios created in southeastern and western parts of the Black Sea by GNOME, oil distribution and connection areas with the coast is known. It is known that the largest oil spill accidents in the Caspian Sea are Tengiz Oil Field Accident (1985) [27], Gas leak and blowout (2008) [28] and Socar Accident (2014) [29]. Unfortunately, it has not been come across to work about the effects of oil spill accident on the biodiversity in the literature. Even if scenarios were created before the accidents for the Caspian Sea, oil spill effects and connection areas could not be found. In order to determine the oil spill area over the sea, beginning with wind, tide and current data; water temperature, salinity and wave values also need to be known, both insitu and long-term. While oil spill model being run, basically in model's software, current data and wind data gathered during the event should be used. If data monitoring is accomplished on long-term, the cost and the oil spill effects on biodiversity in the Caspian Sea's special coastal areas will be clearly understood.

5. CONCLUSION: Future Plans

The priorities in this study were to determine the effects on sea ecosystem, reveal threats against biodiversity, and reduce short and long-term damages. The ever-growing demand for energy in the modern world continues to increase the risks of major oil spills during the long travel of this natural resource along global sea routes. Despite all these studies, oil spill accidents are the inevitable result of oil rigs, storage and shipment. Both of them, Caspian & Black Sea, are under the risk of increasing ship traffic and oil transfer. There are many research programs, which will be investigated in the future for waste minimization in the Caspian Sea [30]. The important ones are given as follow: a) The first one is to identify the point sources of pollution in the Caspian Sea. This includes the pollution from all industries, commercial places and cities around the Caspian Sea. b) The second task is to identify the non-point pollution sources as much as possible, and to characterize them as point sources of pollution. c) The third program is to determine the contribution of each point source pollutant including domestic, industrial, business offices and non-point sources in the Caspian Seaboard and to prepare dispersion map of pollutant sources. d) The forth task is to investigate the effect of these pollution on the aquatic life of the Caspian Sea. e) The last plan is to measure the amount of oil pollution in the Caspian Sea.

Against a background of high natural variability, more subtle damage inflicted by an oil spill, such as a downturn in breeding success, productivity or biodiversity, can be difficult to detect. It is certain that there will not be any life form which can escape from long-term pollution, if humankind won't learn to be responsible about this matter.

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References

[1] Curkovic, S. 2012. Sustainable Development - Authoritative and Leading Edge Content for Environmental Management, 600 p., InTech. ISBN 978-953-51-0682-1. DOI: 10.5772/2562.

[2] ITOPF. 2013. *Effects of Oil Pollution on the Marine Environment*, Technical Information Paper, http://www.iopcfund.org/publications.htm (Accessed 26 May 2015)

[3] Environmental Protection Agency (EPA). 1999. *Profile of the Oil and Gas Extraction Industry, Understanding Oil Spills And Oil Spill Response,* Washington, D.C. U.S. Government Printing Office. www.epa.gov (Accessed 4 January 2015)

[4] Anyanova, E. 2012. *Oil Pollution and International Marine Environmental Law*, in Chapter 2: Sustainable Development - Authoritative and Leading Edge Content for Environmental Management, InTech. ISBN 978-953-51-0682-1. DOI: 10.5772/2562.

[5] Aladin, N.&Plotnikov, I. 2004. *The Caspian Sea. Lake Basin Management Initiative*, Thematic Paper, pp.22-23.

[6] Kostianoy, A.G.and Kosarev, A. N. 2005. *The Caspian Sea Environment*, Springer, pp. 52-54.

[7] Pourkazemi, M. 2006. Caspian Sea sturgeon Conservation and Fisheries: Past, present and Future, *Journal of Applied Ichthyology*. **22,** 12-16.

[8] Kasymov, A.G. 1994. *Ecology of the Caspian Sea*, Baku, 146 p. (in Russian).

[9] Jafari, N. 2010. *Review of pollution sources and controls in Caspian Sea region, Journal of Ecology and the Natural Environment*, **2**, 25-29.

[10] Aubrey, D.G. 1994. Conservation of biological diversity of the Caspian Sea and its coastal zone. A proposal to the Global Environment Facility, *Report to GEF*, 250 pages.

[11] Dumont, H.J. 1998. The Caspian lake: History, biota, structure, and function, *Limnology and Oceanography,* **43 (1),** 44-52.

[12] Ivanov, V.P. 1997 *The Caspian Sea Fishery*, White Book, Astrakhan, 134 p.

[13] Ivanov, V.P. 2000. *Biologicheskiye Resursy Kaspiyskogo Morya*, Caspian Fishery Research Institute: Astrakhan.

[14] Mamaev, V. 2002. *The Caspian Sea*, (enclosed and with many endemic species), EEA, Europe's biodiversity, Seas around Europe, Caspian Environment Programme (CEP): http://www.caspianenvironment.org/ (Accessed 26 June 2015)

[15] Daskalov, G.M.&Mamedov, E.V. 2007. *Integrated fisheries assessment and possible causes for collapse of anchovy kilka in the Caspian Sea*, ICES Journal of Marine Science, pp. 503-511.

[16] Ilgar, R.&Güven, K.C. 2007. Çanakkale Boğazı petrol kirlilik düzeyinin saptanması. *Marmara Coğrafya Dergisi*, **15**, 117-130 (in Turkish).

[17] Artüz, M.L. 1991. Petrol Kirlenmesi Açısından Denizlerimizde Durum. *M. B. B. Natural Resources,* **12(1)** (in Turkish).

[18] National Oceanic and Atmospheric Administration 2001a. *User's Manual, General NOAA Oil Modeling Environment*, Coast Guard National. http://response.restoration.noaa.gov/ (Accessed 26 June 2015)

[19] National Oceanic and Atmospheric Administration 2001b. *User's Guide and Examples, General NOAA Oil Modeling Environment*, Coast Guard National. http://response.restoration.noaa.gov/ (Accessed 26 June 2015)

[20] National Oceanic and Atmospheric Administration 2015. Office of Response and Restoration, National Ocean Service, http://response.restoration.noaa.gov/ (Accessed 26 June 2015)

[21] Beegle, C.J. and O'Connor, C. 2005. GNOME data formats and associated example data files. NOAA Office of Response & Restoration, Emergency Response Division, Seattle.

[22] Brovchenko, I., Kuschan, A., Maderich, V., Shliakhtun, M., Yuschenko, S., Zheleznyak, M. 2003. The modelling system for simulation of the oil spills in the Black Sea, Building the European Capacity in Operational Oceanography Proceedings of the Third International Conference on EuroGOOS, Athens, Greece.

[23] Başar, E., Köse, E., Güneroglu, A. 2006. Finding risky areas for oil spillage after tanker accidents at Istanbul strait. *Int. J. Environment and Pollution*; **27(4)**: 388-400.

[24] Başar, E. 2010. Weathering and oil spill simulations in the aftermath of tanker accidents at the junction points in the Marmara Sea. *Fresenius Environmental Bulletin*, 19: 260-65.

[25] Fingas, M. 2012. *The Basics of Oil Spill Cleanup*, 3rd ed.; CRC Publisher: USA; pp.286.

[26] Rehder, G., Eckl, R., Elfgen, M., Falenty, A., Hamann, R., Kähler, N., Kuhs, FW., Osterkamp, H., Windmeier, C. 2012. Methane hydrate pellet transport using the self-preservation effect: A techno-economic analysis. *Energies*, ***5*****(7):** 2499-2523.

[27] Khakimov, M. and Tabigaty, K. 2012. Well "Tengiz-37" is a 21st century bomb (Kazakhstan), Business & Human Rights Resource Centre, http://business-humanrights.org (Accessed 25 April 2015).

[28] Gismatullin, E. 2008. BP Shuts Down Two Azeri Oil Platforms After Gas Leak, http://www.bloomberg.com/apps/news (Accessed 26 June 2015)

[29] OE Press .2014. *Socar Accident*. Retrieved from (www.oedigital.com/vessels/item/)

Romanova, L. and Tesyomnikova, E. 2000. Putin defends Russian interests in the Caspian, Nezavisimaya Gazeta.

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Occurrence of selected micro-pollutants in the surface water: a case study on effect of a non-treated wastewater discharged into the Danube River, Vojvodina Province, Serbia

B. Skrbic[*], I. Antić, N. Djurišić-Mladenović, D. Tadić

Faculty of Technology, University of Novi Sad, 21000, Novi Sad, Serbia
*Corresponding author: Email: biljana@tf.uns.ac.rs

Abstract

The aim of the study was to analyze contents and temporal trends of 11 perfluorinated compounds, 3 pharmaceutically active compounds: carbamazepine, diclofenac and ibuprofen; a polar pesticide: diuron; 16 US EPA polycyclic aromatic hydrocarbons and a pyrethroid–organochlorine insecticide: cypermethrine, in 8 composite wastewater samples which were collected directly at discharge point into the Danube River, at the 24 h-time period, and in 12 composite surface water samples collected from Danube down and up stream of the wastewater discharged point during 30 days period. Contribution of wastewater discharged to the content of the investigated 32 micro-pollutants in the downstream surface water in proximity was also assessed. All the obtained results were compared with the literature available data. This is the first study reporting the occurrence of perfluorinated compounds in the Serbian surface water, which might be regarded as important baseline for future monitoring.

Keywords: micropollutants; surface water; wastewater discharge; middle Danube.

1. INTRODUCTION

Emerging contaminants can be defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment, but has the potential to enter the environment and cause known or suspected adverse ecological and human health effects. Generally, these chemicals are produced on a large scale worldwide, and they are used in a wide range of applications, being indispensable to our modern society [1]. Among them carbamazepine, diclofenac and ibuprofen belong to the group of pharmaceuticals which are a large and diverse group of compounds designed to prevent, cure and treat diseases and improve health [2]. Concern about perfluorinated compounds (PFCs) belonging to a class of emerging persistent organic pollutants is growing because they are globally distributed, environmentally persistent, bioaccumulative and potentially harmful [3]. Among them, metabolic products such as perfluorooctanoate (PFOA) and perfluorooctansulfonate (PFOS) have received more attention because of their ubiquitous presence in the environment [4]. In December 2006, the European Parliament and the Council decided to restrict marketing and use of PFOS [5]. Additionally, PFOS is included in a list of so called priority substances regulated by the Water Framework Directive. For PFOA, in the EU, regulatory restrictions similar to the ones in place for PFOS are currently under discussion until the end of 2015 [6] and emissions and use of PFOA in products were voluntarily planned to be eliminated [7]. PFCs, which are consisted of a fully fluorinated hydrophobic alkyl chain attached to a hydrophilic end group, have been widely used for over 50 years, in several industrial and household applications due to their unique physicochemical properties: thermal stability and oxidative resistance. They are extensively used in surfactants, fire-fighting foams, food packing

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paper, textile, carpet and leather treatment. Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants of concern since many of them and many PAH mixtures exhibited mutagenic and/or carcinogenic properties [8]. PAHs are ubiquitous and their sources and fate have been extensively investigated in different environmental compartments [9-14]. However, there is a concern in the determination of PAHs in water since many natural water bodies are used as potable water supplies after treatment. Many environmental agencies have established very low maximum concentration levels of PAHs for potable and fresh waters. For example, US EPA sets maximum acceptable concentration (MAC) of 0.2 μg L^{-1} for benzo[*a*]pyrene in drinking water. Serbian legislation sets the level of 130 mg L^{-1} for naphthalene, 0.27 mg L^{-1} for benzo[*a*]pyrene, 17 μg L^{-1} for both benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, and 8.2 μg L^{-1} for benzo[*ghi*]perylene in surface water [15]. There are many sources of PAHs to natural water, such as wastewater from municipal and industrial activities, atmospheric deposition, leachate from solid waste disposal dumps etc. Diuron is a herbicide and a suspected human carcinogen, widely used around the world although its use is banned or restricted in some countries e.g. in Sweden, Denmark, Germany and UK due to its harmful effects on the environment and human health. Since diuron degrades slowly in water, it is quite persistent in the environment [16].

The threat posed by the release of those contaminants through wastewater treatment plant effluents is particularly worrisome in streams or small rivers, where the dilution capacity of the receiving freshwater ecosystem is small [17]. Although the Danube River, as the largest river in Serbia, has the greatest dilution capacity, the worrisome problem is untreated discharged wastewater for only 5% [18,19] of all wastewater are treated in Serbia. Since the surface water samples were collected upstream and downstream of the wastewater discharge point into the Danube River, the results obtained in this study were used to assess the impact of 32 investigated micro-pollutants on surface water. Also, the objective of this study was to identify for the first time the level of 11 investigated PFCs in the Serbian part of the Danube River. To our best of knowledge there is no published data regarding the concentration of 11 PFCs in surface water of the Danube in Balkan countries.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

Eleven PFCs: perfluorobutane sulfonic acid (PFBS); perfluorooctansulfonate PFOS; perfluoro-octane (PFOSA); perfluorobutyric acid (PFBA); perfluorohexanoic acid (PFHxA); perfluoro-heptanoic acid (PFHpA); perfluorooctanoate PFOA; perfluorononanoic acid (PFNA); perfluoro-decanoic acid (PFDA); perfluoroundecanoic acid (PFUndA); perfluorododecanoic acid (PFOdA) were obtained from Chiron AS (Trondhem, Norway). Eight surrogate compounds (CUS-MPFC-MXA Mass-Labelled PFCAs and PFASs Solution/Mixture) and nine internal standards (MPFAC-MXA Mass-Labelled PFCAs and PFASs Solution/Mixture) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). A mixed standard solution of 16 US EPA priority PAHs (naphthalene (Nap), acenapthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene BbF, benzo[*k*]fluoranthene BkF, benzo[*a*]pyrene BaP, indeno[1,2,3-cd] pyrene (InP), dibenzo[ah]anthracene (DB), benzo[*ghi*]perylene (Bghi) in dichlormethane /benzene (1:1) was obtained from LGC Standard, Germany. Deuterated PAH d_{12}-benzo[*a*]pyrene (d_{12}-BaP) in acetonitrile, obtained from Chiron AS, Norway, was used as a surrogate standard, 1,3,5-triphenylbenzene (Supelco, USA) was used as an internal standard. Waters Oasis HLB Plus LP (225 mg, 60 μm) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). Diclofenac acid and ibuprofen, were purchased from Dr. Ehrenstorfer, Germany.

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Carbamazepin and diuron, were purchased from Sigma Aldrich, Switzerland. Grade GF/F glass microfiber filters (0.47 μm) were purchased from Whatman International Ltd (Maidstone, Kent, UK). Ultra-pure water (resistivity 18.2 MΩcm) was obtained from Milli-Q system (Millipore, Molsheim, France). Methanol and ammonium acetate, both LC-MS grade, were purchased from J.T. Baker (Deventer, Netherlands), glacial acetic acid (p.a.) was obtained from LTG Promochem (Wesel, Germany) while n-hexane (Fisher Chemical, UK) and dichlormethane (AppliChem Panreac ITW Reagents, Spain) were both HPLC grade. Silica gel for chromatography was obtained from Carlo Erba Reagents (France), while phosphate buffer was obtained from Acros Organics (Belgium). Sodium chloride and anhydrous sodium sulphate were purchased from Fluka Analytical (Germany).

2.2. Quality assurance/quality control

All methods were validated by "in-house" quality control procedure for purpose of present study. Recovery values for PAHs were in the range from 60% to 127% for surface water samples and from 63% to 118% for wastewater samples. For cypermetrine recovery values were 107% and 81% for surface and wastewater samples, respectively. For PFCs recovery values were in range from 65% to 121%, while for diclofenac, ibuprofen, carbamazepine and diuron recovery values were 108%, 97%, 79% and 75%, respectively, for both type of water samples.

Limits of quantification (LOQs) for PAHs for surface water samples were in the range 0.02-0.90 ng L^{-1}, while for wastewater samples were 0.04-1.8 ng L^{-1}. For cypermetrine LOQ values were 3.9 ng L^{-1} and 7.9 ng L^{-1} for surface and wastewater samples, respectively. LOQ for PFCs were in the range from 0.04 ng L^{-1} to 0.63 ng L^{-1} while for diclofenac, ibuprofen, carbamazepine and diuron were 1.5 ng L^{-1}, 22 ng L^{-1}, 0.35 ng L^{-1} and 0.54 ng L^{-1}, respectively, for both, surface and wastewater samples.

2.3. Sampling

The sampling was carried out during the winter season. Qualified and well-trained person from public water management company "Vode Vojvodine" Novi Sad collected the samples. The 12 composite surface water samples were taken downstream (SWD) and upstream (SWU) from the wastewater discharge point, while 8 wastewater samples were collected directly at discharge point, at the 24 h-time period. The wastewater samples were collected in the polypropylene bottles (500 mL; filled to the top), sealed, stored in a refrigerator and transport to the lab where they were stored at 4^{o} C until further processing. Field blanks were collected by filling the laboratory water (Milli-Q) from the field blank bottle into the sampling device, letting to stand for 5 min, and then transferring this water back to the field blank bottle. Teflon bottles, teflon-lined caps and any suspect fluoropolymer materials were avoided throughout the analysis, in order to avoid contamination of the samples.

The wastewater discharge point is located on the bank of the Danube flow between Novi Sad (the second largest town in Serbia) and Belgrade (the capitol of Serbia). It has been used to discharge the municipality wastewater collected from four towns (Inđija, Stara Pazova, Nova Pazova and Batajnica, with approximately 150000 inhabitants in total) and as well as from small villages located in this area without any pre-treatment directly into the Danube River.

2.4. Sample preparation, cleanup and analysis

All water samples were filtered through 0.47 μm glass microfiber filters (GF/F), previously pre-conditioned by passing 10 mL of methanol and 10 mL Milli-Q water. Before filtration the samples were spiked with surrogate standards. Analytical method for determination of PFCs, ibuprofen, carbamazepine, diclofenac and diuron in wastewater and surface water samples were developed by Duong et al. [20]. Briefly, all samples (500 mL for surface water and 300 mL for wastewater) were extracted by SPE with Oasis HLB cartridges. The SPE cartridges were first preconditioned by

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passing 5 mL of methanol and 10 mL of Milli-Q water at a flow-rate of 10 mL/min. Elution was performed with 5 mL of methanol at a flow rate 1 drop/s. Extracts were concentrated to 500 μL under a gentle nitrogen stream and were spiked with internal standard prior to determination step. Concentration of PFCs, ibuprofen, carbamazepine, diclofenac and diuron in samples were analyzed using ultra high-performance liquid chromatography (UHPLC) Accela system (pump and autosampler) interfaced with a TSQ Vantage triple quadrupole mass spectrometer (MS/MS) equipped with heated-electrospray ionization probe HESI-II (Thermo Thermo Fisher Scientific, San Jose, United States). Separation of analytes was achieved using a Hypersil GOLD^{TM} (50 mm x 2.1 mm i.d., 1.9 μm) column (Thermo Fisher Scientific). The gradient was composed of eluent A containing water/acetic acid (99:1, v/v), and eluent B containing of methanol/acetic acid (99:1, v/v). Eluent A contained 10 mM ammonium acetate, while elunt B contained 5 mM ammonium acetate.

The applied sample preparation and determination method for PAHs and cypermetrine is slightly modified from Hanh et al. [21]. Namely, thirty grams of sodium chloride was added into separatory funnel contained the requested aliquot of the water sample (1000 mL for surface water and 500 mL for wastewater). The pH of the sample was adjusted at 7.0 with a phosphate buffer. The samples were twice extracted with 100 mL and 50 mL of dichloromethane for 10 minutes each. Extracts were combined and dehydrated by passing through an anhydrous sodium sulphate column. In the case of surface water, the extract was concentrated with a rotary evaporator to about 5 mL. Then, 20 mL of hexane was added and re-concentrated to 5 mL, and finally to exact 1 mL under a gentle nitrogen stream prior the analysis by gas chromatography mass spectrometry. Whereas, dehydrated extracts of wastewater samples (after anhydrous sodium sulphate column) were concentrated to 2 mL, followed by cleanup on the silica gel column: two fractions obtained by elution with hexane and hexane/dichlormethane, respectively, were concentrated to exact 500 μL under a gentle nitrogen stream before analyze. The PAHs and cypermetrine were analyzed by gas chromatograph with mass selective detector (GC MS-Agilent 7809B-5977A, Germany) equipped with a HP-5MS column (30 m×0.25 mm i.d., 0.25 μm film thickness), using helium as the carrier gas. The MS was operated in the electron impact ionization mode and the mass scanning was under the selected ion monitoring (SIM) mode.

3. RESULTS AND DISCUSSION

Compounds detected in the upstream and downstream surface water samples are presented in Table 1, while those in wastewater samples are given in Table 2.

Cypermethrine was not detected in any of the analysed water samples. Limits of quantification were 3.9 and 7.9 ng L^{-1} for surface and wastewater, respectively.

Among 16 PAHs Ace, Flu, BaA, Chr, BkF, BbF, BaP, InP and DB were not detected in surface water samples. The detected concentrations in surface water ranged between 9.3 and 54 ng L^{-1} for 2-ring PAH (Nap), 1.2–20 ng L^{-1} for sum of the 3-ring PAHs (Acy, Fl, Phe, and Ant), 6.3 ng L^{-1} for 4-ring PAH (Pyr) detected only in SWU (12.11) and 8.7 ng L^{-1} for 6-ring PAH (Bghi) detected only in SWU (12.11) (Table 1). No 5-ring PAHs (BaP, BbF, BkF) were detected in surface water samples, whereas Nap and Fl were the most frequently detected PAHs with the mean values of 28 ng L^{-1} and 4.2 ng L^{-1}, accounted for 45-96% and 4-41% of the total PAHs concentration, respectively.

Moreover, the low-molecular-weight PAHs (2- and 3-ring PAHs) were only detected PAHs in all samples except in sample (12.11.), in which Pyr and Bghi were detected also, showing that low-molecular-weight PAHs are abundant in the Danube River. The Final Report of Joint Danube Survey 3 [22] stated that summed concentrations (Σ16 US EPA PAHs) of free dissolved PAHs in the Danube River ranged between 11 ng L^{-1} and 45 ng L^{-1} in a sampling area length of 2500 km, which coincided with the range of Σ16 US EPA PAHs levels found in this study (14-64 ng L^{-1}).

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Mean concentrations from both studies shows much smaller PAHs presence than in Yangtze River Delta (China): 3717 ng L^{-1} [23] and in Daliao River (China) watershed composed of the Hun River, Taizi River, and Daliao River: 6471 ng L^{-1} [24].

Table 1. Detected concentrations (ng L^{-1}) and temporal trends of micro-pollutants in the Danube surface water samples upstream (SWU) and downstream (SWD) from the wastewater discharge point

Compound	SWU 12.11.	SWD 12.11.	SWU 20.11.	SWD 20.11.	SWU 21.11.	SWD 21.11.	SWU 25.11.	SWD 25.11.	SWU 27.11.	SWD 27.11.	SWU 29.11.	SWD 29.11.
Acy	<0.06	<0.06	0.30	0.50	<0.06	0.40	0.90	1.1	1.0	0.60	0.40	1.4
Fl	2.7	1.2	2.0	1.4	0.30	4.2	2.8	3.9	7.7	3.1	11	9.5
Phe	7.6	<0.07	0.30	<0.07	0.30	5.9	<0.07	5.7	1.0	7.0	4.3	7.1
Ant	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	3.7
Pyr	6.3	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Bghi	8.7	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62	<0.62
Nap	21	30	30	16	9	21	48	54	27	28	31	28
PFHxA	5.9	11	8.4	12	11	10	11	8.4	9.5	8.9	12	12
PFOA	8.9	11	14	14	13	11	12	14	12	12	11	13
PFOS	3.2	3.0	3.8	3.5	4.1	15	5.3	6.3	4.6	3.4	9.5	12
PFNA	1.5	3.7	1.5	5.0	4.2	3.7	1.4	1.7	1.6	2.0	2.4	4.6
PFDA	2.1	2.4	2.0	<0.58	2.0	<0.58	4.4	1.9	1.7	2.1	<0.58	<0.58
PFUdA	1.0	<0.39	1.0	<0.39	<0.39	<0.39	<0.39	0.9	<0.39	<0.39	<0.39	4.6
Diuron	3.3	2.3	3.1	3.3	3.2	3.2	2.8	3.0	2.9	3.0	3.7	2.0
Carbamazepine	7.4	6.7	7.5	7.4	6.8	8.3	7.3	8.4	8.0	8.2	9.5	9.8
Ibuprofen	37	44	<22	<22	<22	78	<22	66	<22	63	<22	57
Diclofenac	46	36	38	44	36	43	37	43	39	43	44	28

Among analysed 16 US EPA PAHs Ace, Ant, BbF, BkF and DB were not detected in wastewater samples. The most prevalent PAHs in wastewater samples were 4-ring and 6-ring PAHs accounted for 14-59% and 15-56% of the total PAHs concentration, respectively (Table 2). Among 4-ring PAHs the most frequent was Pyr and among 6-ring PAHs it was Bghi. The average concentration of the Σ16 US EPA PAHs in the wastewaters (634 ng L^{-1}) was higher than in the surface waters (39 ng L^{-1}). Considering concentrations of individual PAHs in SWU and SWD samples in 55% of all cases individual PAH concentration was higher in SWD than in SWU samples, indicating no influence of discharge plant to the Danube River.

Out of 11 analysed PFCs four of them (PFNA, PFOS, PFOA and PFHxA) were detected in all surface water samples, whereas PFDA and PFUdA were detected sporadically. PFOA and PFHxA were the most abundant compounds in surface water samples, with the mean concentration of 12 ng L^{-1} and 10 ng L^{-1}, generally accounting for 25–35% and 28–46% of the total PFCs concentrations, respectively. This distribution is similar to data reported for surface water in the Europe [25,26] and Sri Lanka [27], where PFOS and PFOA were dominant but PFNA was a minor component, but different to those in river from Japan and Vietnam where PFOA and PFNA were more abundant than PFOS [28,20]. In particular, PFOA is used as adjuvant in the production of fluoropolymers such as Teflon® or similar products, and occurs in these applications as aqueous and gaseous process emission [26]. The Final Report of Joint Danube Survey 3 reports 8.1 ng L^{-1} as average concentration of PFOA in the Danube River downstream Budapest and 7.2 ng L^{-1} as average concentration of PFOS in the Danube River in Szob before Budapest. Interestingly, PFHxA was

detected in relatively high concentration (relative to other detected PFCs) in this study but not in the other mentioned papers. PFOS and PFOSA were only detected PFCs in wastewater samples. Since PFOSA was not detected in surface water samples it could be concluded that untreated wastewater does not have influence on PFOSA content in the Danube River. A similar conclusion can be drawn for PFOS, since its mean value for upstream and downstream the Danube surface water samples (6.1 ng L^{-1}) is almost 2.5 time higher than in wastewater samples (2.5 ng L^{-1}).

Comparing individual PFCs concentrations in surface water samples upstream and downstream from discharge point, trend similar to the one observed for PAHs was obtained. Namely, in about half of compared cases (52%), individual PFCs concentrations were lower in downstream samples than in upstream samples.

Table 2. Detected concentrations (ng L^{-1}) and temporal trends of micro-pollutants in wastewater samples

Compound	WW 12.11.	WW 21.11.	WW 26.11.	WW 27.11.	WW 28.11.	WW 29.11.	WW 30.11.	WW 01.12.
Acy	7.1	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Fl	12	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Phe	27	<0.10	2.6	31	13	7.7	6.2	174
Flu	5.3	9.7	7.5	13	63	74	66	150
Pyr	51	34	27	16	224	274	244	393
BaA	<0.24	6.6	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
Chr	<0.36	18	14	22	29	32	30	50
BaP	<1.8	<1.8	<1.8	<1.8	42	50	44	87
InP	<1.0	<1.0	<1.0	<1.0	75	105	91	163
Bghi	63	43	33	14	374	441	411	602
Nap	235	5.1	4.6	14	9.7	0.8	6.5	23
PFOS	<0.32	<0.32	<0.32	2.5	1.2	3.5	2.7	<0.32
PFOSA	2.8	6.1	7.4	<0.93	3.9	2.4	2.6	2.7
Carbamazepine	43	70	33	41	30	29	36	42
Ibuprofen	9846	8220	8356	8549	6976	6143	8405	8700
Diclofenac	667	656	685	730	520	479	679	690

Diuron was not detected in wastewater (<0.54 ng L^{-1}), but showed rather uniform level (2.0-3.7 ng L^{-1}; mean value 3.0 ng L^{-1}) in the surface water which is far smaller than it is presented in the study of Loos et al. [26], who reported the content of 41 ng L^{-1} for more than 100 individual water samples from over 100 rivers from 27 European Countries. Higher contents of carbamazepine, ibuprofen and diclofenac (mean concentrations of 41 ng L^{-1}, 8149 ng L^{-1} and 638 ng L^{-1}, respectively) were obtained in wastewaters than in the surface waters (mean concentrations of 7.9 ng L^{-1}, 58 ng L^{-1} and 40 ng L^{-1}, respectively). In 75% of all studied cases concentration of carbamazepine, ibuprofen and diclofenac in downstream samples were higher than in upstream samples. From all the studied micro-pollutants, only for pharmaceuticals the wastewater discharge seemed to have the influence on their concentrations in the Danube River, especially for ibuprofen because in every surface water sample in which ibuprofen was detected its concentration was higher in downstream than in upstream samples. Direct wastewater discharge is one of the main sources of pharmaceuticals compounds in fresh water ecosystems [2]. The presence of pharmaceuticals in surface waters, and therefore in other environmental compartments, may be affected by several processes, such as photolysis, hydrolysis, sorption and biodegradation. Understanding partitioning

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behaviour of contaminants in the biological compartment, and the role of biota in the removal of these bioactive compounds from surface water is of critical importance to studying their ecological impact [17]. Loos et al. [26] detected much higher average concentrations in European rivers for carbamazepine (248 ng L^{-1}) and ibuprofen (395 ng L^{-1}) but less for diclofenac (17 ng L^{-1}), similarly Huerta et al. [17] in River Segre (Spain) report higher mean concentrations for carbamazepine (25 ng L^{-1}) and ibuprofen (141 ng L^{-1}) but less for diclofenac (25 ng L^{-1}). The Final Report of Joint Danube Survey 3 [22] also reports higher amount of carbamazepine (26 ng L^{-1}) and less of diclofenac (13 ng L^{-1}) in the Danube River.

4. CONCLUSION

The present study contributes to the previous EU studies on the occurrence of micro-pollutants in the Danube River water. The results obtained for PAHs, PFOA and PFAS are in rather good agreement with the results from the wider EU survey conducted for the Danube River, while the levels detected for pharmaceuticals and diuron differed from data reported. The results gave an additional prove that discharge of municipal wastewaters is the main source of pharmaceuticals and other polar contaminants in the Danube River.

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5. REFERENCES

[1] Da Silva, B. F., Ferreira D, B., Jelic, A., López-Serna, R., Mozeto, A., Petrovic, M., Barceló, D., 2011. Occurrence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro River Basin, Spain. *Chemosphere*, **85 (8)**, 1331–1339.

[2] Petrović, M., Škrbić, B., Živančev, J., Ferrando-Climent, L., Barcelo, D., 2014. Determination of 81 pharmaceutical drugs by high performanceliquid chromatography coupled to mass spectrometry with hybridtriple quadrupole–linear ion trap in different types of water in Serbia. *Science of the Total Environment*, **468**, 415–428.

[3] Arvaniti, O. S., Stasinakis, A. S., 2015. Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. *Science of the Total Environment*, **524-525**, 81–92.

[4] Pérez, F., Llorca, M., Köck-Schulmeyer, M., Škrbić, B., Oliveira, L. S., Martinello, K. B., Al-Dhabi, N. S., Antić, I., Farré, M., Barceló, D., 2014. Assessment of perfluoroalkyl substances in food items at global scale. *Environmental Research*, **135**, 181–189.

[5] EU, 2006. European directive 2006/122/EC of the European parliament and council of 12 December 2006. Amending for the 30th time council directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the member states relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates). *Official Journal of the European Union*, **OJ L 372**, 32-34.

[6] ECHA., 2014. European Chemicals Agency Submitted Restriction (accessed 01.03.15.). http://echa.europa.eu/documents/10162/3b6926a2-64cb-4849- b9be-c226b56ae7fe.

[7] Lindim, C., Cousins, I.T., Van Gils, J., 2015. Estimating emissions of PFOS and PFOA to the Danube River catchment and evaluating them using a catchment-scale chemical transport and fate model. *Environmental Pollution*, **207**, 97-106.

[8] Wang, X. T., Chen, L., Wang, X. K., Lei, B. L., Sun, Y. F., Zhou, J., Wu, M. H., 2015. Occurrence, sources and health risk assessment of polycyclic aromatic hydrocarbons in urban (Pudong) and suburban soils from Shanghai in China. *Chemosphere,* **119**, 1224–1232.

[9] Škrbić, B., Miljević, N., 2002. An evaluation of residues at an oil refinery site following fires. *Journal of Environmental Science and Health, part A-Toxic/Hazardous Substances & Environmental Engineering,* **37 (6)**, 1029-1039.

[10] Golobočanin, D., Škrbić, B., Miljević, N., 2004. Principal component analysis for soil contamination with PAHs. *Chemometrics and Intelligent Laboratory Systems,* **72 (2)**, 219-223.

ISBN: 978-960-6865-94-7

[11] Škrbić, B., Cvejanov, J., Đurišić-Mladenović, N., 2005. Polycyclic aromatic hydrocarbons in surface soils of Novi Sad and bank sediment of the Danube River. *Journal of Environmental Science and Health, part A-Toxic/Hazardous Substances & Environmental Engineering*, **40 (1)**, 29-42.

[12] Škrbić, B., Cvejanov, J., Đurišić-Mladenović, N., 2008. Polycyclic aromatic hydrocarbons in products of a beet sugar factory in Vojvodina: levels and intakes, *Polycyclic Aromatic Compounds*, **28 (4-5)**, 348-361.

[13] Škrbić, B., Sudji, J., Vuković, R., 2008. Contents of polycyclic aromatic hydrocarbons in products of the Serbian beet sugar factory. *Zuckerindustrie*, **133 (1)**, 31-35.

[14] Škrbić, B., Đurišić-Mladenović, N., 2009. Levels of PAHs in soil samples from the vicinity of oil refinery Novi Sad-Serbia, *Kuwait Journal of Science & Engineering*, **36 (1A)**, 63-75.

[15] Official Bulletin of the Republic of Serbia, 24/14, Maximum allowed contents of contaminants in surface water, pp. 1–9.

[16] Huovinen, M., Loikkanen, J., Naarala, J., Vähäkangas, K., 2015. Toxicity of Diuron in Human Cancer Cells. *Toxicology in Vitro*, **29 (7)**, 1577–1586.

[17] Huerta, B., Rodriguez-Mozaz, S., Nannou, C., Nakis, L., Ruhi, A., Acuna, V., Sabater, S., Barcelo, D., 2015. Determination of a broad spectrum of pharmaceuticals and endocrine disruptors in biofilm from a wastewater treatment plant-impacted river. *Science of the Total Environment*, **540**, 241–249.

[18] Terzić, S., Senta, I., Ahel, M., Gros, M., Petrović, M., Barcelo, D., Müller, J., Knepper, T., Martí, I., Ventura, F., Jovancić, P., Jabucar, D., 2008. Occurrence and fate of emerging wastewater contaminants in Western Balkan Region. *Science of Total Environment*, **399**, 66–77.

[19] Schröder1, P., Helmreich, B., Škrbić, B., Carballa, M., Papa, M., Pastore, C., Emre, Z., Oehmen, A., Langenhoff, A., Molinos, M., Dvarioniene, J., Huber, C., Tsagarakis, K. P., Martinez-Lopez, E., Meric Pagano, S., Vogelsang, C., Mascolo, G., 2016. Status of hormones and painkillers in wastewater effluents across several European states—considerations for the EU watch list concerning estradiols and diclofenac. *Environmental Science and Pollution Research*, DOI 10.1007/s11356-016-6503-x.

[20] Duong, H. T., Kadokami, K., Shirasaka, H., Hidaka, R., Chau, H. T. C., Kong, L., Nguyen, T. Q., Nguyen, T. T., 2015. Occurrence of perfluoroalkyl acids in environmental waters in Vietnam. *Chemosphere*, **122**,115–124.

[21] Hanh, D. T., Kadokami, K., Matsuura, N., Trung, N. Q., 2013. Screening analysis of a thousand micro-pollutants in Vietnamese rivers. *Southeast Asian Water Environment*, **5**, 195-202.

[22] The Final Report of Joint Danube Survey 3, 2015. Joint Danube Survey 3, a comprehensive analysis of Danube water quality. Published by ICPDR e International Commission for the Protection of the Danube River. http://www.danubesurvey.org/results (accessed 27.05.15).

[23] Chen, B., Xuan, X., Zhu, L., Wang, J., Gao, Y., Yang, K., Shen, X., Lou, B., 2004. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Water Research*, **38 (16)**, 3558–3568.

[24] Guo, W., He, M., Yang, Z., Lin, C., Quan, X., Wang, H., 2007. Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter andsediment from Daliao River Watershed, China. *Chemosphere*, **68 (1)**, 93–104.

[25] Mclachlan, M. S., Holmstrom, K. E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European Continent. *Environmental Science and Technology*, **41 (21)**, 7260–7265.

[26] Loos, R., Locoro, G., Huber, T., Wollgast, J., Christoph, E. H., De Jager, A., Gawlik, B. M., Hanke, G., Umlauf, G., Zaldivar, J. M., 2008. Analysis of perfluorooctanoate (PFOA) and other perfluorinated compounds (PFCs) in the River Po Watershed in N-Italy. *Chemosphere*, **71 (2)**, 306–313.

[27] Guruge, K. S., Taniyasu, S., Yamashita, N., Manage P. M., 2007. Occurrence of perfluorinated acids and fluorotelomers in waters from Sri Lanka. *Marine Pollution Bulletin*, **54 (10)**, 1667–1672.

[28] Murakami, M, Imamura, E., Shinohara, H., Kiri, K., Muramatsu, Y., Harada, A., Takada, H., 2008. Occurrence and sources of perfluorinated surfactants in Rivers in Japan. *Environmental Science and Technology*, **42 (17)**, 6566–6572.

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Environmental threats from high enthalpy fluid storage in geothermal power systems

G. Piperidis[1], Z. S. Nivolianitou[2*], E. Kondili[1]

[1] Optimization of Production Systems Laboratory, Mechanical Engineering Department, TEI of Piraeus, PO Box 41046, Athens 12201, Greece.
[2] Systems Reliability & Industrial Safety Laboratory, Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, National Centre of Scientific Research 'Demokritos', Aghia Paraskevi 15310, Greece.
*Corresponding author: Email: zoe@ipta.demokritos.gr

Abstract

A significant place among renewal energy sources holds the geothermal energy, the utilization of which for electricity generation has been commercially since 1913. As a renewable energy source, geothermal energy can enhance a low carbon economy and strengthen independency from imported fuels, allowing for a sustainable national energy balance. In Greece geothermal energy has been used already in the early '90s only for direct utilization. Despite the large high-enthalpy geothermal potential of the Greek reservoirs the use of this natural resource has not been persistent for electricity production in the country. One of the reasons was severe technical problems, which led to public aversion regarding its use. The aim of this paper is to study, through a specific risk analysis approach, potential risks and accidents in a geothermal installation in order to make the latter more reliable and environmentally friendly offering at the same time a different perspective to public and influencing positively its awareness on this kind of facilities.

Keywords: geothermal energy; risk analysis; fluid reinjection; environmental hazards; geothermal Power Plants

1. INTRODUCTION

During the last years, the continuously rising energy demand is very evident. This can be explained by the sharp growth of the developing countries, as well as the improvement of living standards in the developed ones. Fossil fuels are the main energy source for most of the countries for several decades. However, the limited inventory of the former and the need for energy independence made most countries to invest gradually into renewable energy sources in order to reduce the share of technologies based on fossil fuels. Renewable resources have an unlimited availability; are –in most cases- equitably distributed around the world; are characterized as clean technologies because they produce very little waste and also have a minimal environmental impact. Moreover, they contribute not only to the reduction of CO_2 emissions but also to other pollutant gas emissions, such as sulfur, nitrogen oxides ad VOCs (volatile organic compounds) fostering both environmental protection, and growth sustainability. This is in line with the future socioeconomic and environmental needs of global economy serving also the Kyoto treaty objectives [1, 2].

A significant place among renewal energy sources holds the geothermal energy, the utilization of which for electricity generation has been commercially since 1913. As a renewable energy source, geothermal energy can enhance a low carbon economy and strengthen independency from imported fuels, allowing for a sustainable national energy balance. Geothermal power can be used as baseload renewable energy twenty four hours a day throughout the year in order to generate

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electricity regardless of the weather variations. Moreover, geothermal energy can fluctuate depending on the country needs and can be flexible to support the intermittent renewable energy resources demands from wind and solar parks. In this context, it can be used to provide the stability of the power grid enhancing the efficiency of the entire system and increasing the security of energy supply against disruptions for geopolitical reasons and fossil fuel's price high votatility[1]. In Greece geothermal energy has been deployed already in the early '90s only for direct utilization. Despite the large high-enthalpy geothermal potential of the Greek reservoirs the use of this natural resource has not been persistent for electricity production in the country. One of the reasons was severe technical problems, which led to public aversion regarding its use.

It is well-known that any power generation scheme is associated with potential environmental and population risks; the same applies to geothermal energy making imperative the necessity to find and underline the risks stemming from its use in order to strengthen safeguards and preserve the acceptability of geothermal facilities and activities. The geothermal fluid itself may contain several non-condensable gases (NCG), such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S). The first is a well-known "climate changing" gas, while the other is highly toxic and dangerous above certain concentrations. Moreover, the presence of silica and boron in the geothermal brine can be hazardous both to people and to the surface environment. For these reasons geothermal fluid reinjection has to be implemented. The reinjection process is a vital part of any geothermal development, affecting directly the success or failure of any geothermal field development. Thus, a reinjection plan should be developed as early as possible in any conceptual study of a geothermal development taking into account that the field characteristics are likely to change with time. The fluid reinjection into the geothermal system during utilization is going to serve two purposes: a) the resource recovery improvement and b) the better management of waste water disposal.

High temperature geothermal resources as well as medium temperature resources can be used to generate electricity through three different kinds of Geothermal Power Plants namely, dry steam, flash and binary power plants. In geothermal power plants, steam is used to drive turbines simular to conventional fossil fuel plants. Howerver, on conventional power plants, steam is produced by boiling water through coal, oil or gas combustion, while in geothermal power plants steam is extracted from the ground. [3]

Electricity generation from geothermal fluids is characterized as new in industry, because the first installations of the kind were sited in the beginning of the last century. Geothermal power plant installation has been effectuated in 24 countries around the world. More specifically, the total Worldwide installed capacity for direct use in 2015 was 12.6 GW and a short term forecasting indicates an 9 GW increase by 2020. [4] Greece can be characterized as rich in geothermal resources, since the greatest part of the country lies in a region with active tectonic plates with rich geothermal content. More specifically, high enthalpy geothermal resources have been identified in the active South Aegean volcanic arc and in the islands of Milos and Nisyros with a proven potential of 250MW. However, no geothermal utilization for electricity has been deployed so far [5].

The aim of this paper is to study, through a specific risk analysis approach, potential risks and accidents in a geothermal installation (fluid storage) in order to make the latter more reliable and environmentally friendly offering at the same time a different perspective to public and influencing positively its awareness on this kind of facilities. Since some Geothermal Power Plants face various operating faults the need to eliminate or decrease potential failures is considerable. The key point in the present paper is a safety analysis determining potential accidents in the storage phase of high enthalpy geothermal fluid and the appropriate remediation actions.

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2. SOURCES OF HAZARD

2.1 General

As the aim of this research is to evaluate the potential environmental impacts during the injection phase of the geothermal fluid and, furthermore, to provide through a safety analysis appropriate remediation actions, some notable efforts in this direction are cited in the following. In 1970 on Achuapan field in El Salvador, the first injection effort has been implemented for environmental reasons, where a high Boron content (~50 ppm) was identified and surface disposal was not admissible [6]. Nowadays, injection seems to be the most favorable solution both environmentally and economically. Geothermal fluid injection is important to a geothermal project for a number of reasons, such as (a) to avoid surface disposal which can cause environmental impact, (b) to support the reservoir pressure, (c) to avoid any ground subsidence, and (d) to benefit from rock matrix heat. Depending on the type of the geothermal system, reinjection can be infield, outfield or a mix of them. For vapor-dominated systems where the water can run out reinjection should be infield, while for hot water and liquid-dominated system a mix of infield and outfield injections is recommended. Through infield reinjection, pressure support is provided and, consequently, drawdown and the potential for subsidence will be reduced. However, outfield reinjection protects the production area from the risk of cold water returns. [7]

It has been noted that the lack of planning for injection early in the development phase usually caused delays in putting power on line and reaching the planned generation level as well [8]. Thus, as it was mentioned above, the injection process is a vital part of any geothermal development, affecting directly the success or failure of any geothermal field development.

2.2 Description of problems actually connected with the injection of waste geothermal fluid

Geothermal fluid does not necessarily require to be injected into the production geothermal reservoir; it could be injected into a different aquifer simply to avoid any environmental impact owing to surface disposal. However, in that case many problems can occur, such as ground subsidence, seismicity or leakage of the injection fluid to the surface due to the injection pressure, despite the fact that injection in a shallower aquifer than the producing reservoir saves drilling cost. On the other hand, injection into the production reservoir could be both beneficial as it was mentioned above but also risky owing to the potential cooling of the production well and the possible adverse impact on the chemistry of the extracted geothermal fluid [9].

The injection of waste geothermal fluid is most of the times connected with a number of problems. The suitability of injection sites is a critical choice for plant operation, production, while the injection within the same fault zone can cause serious cooling. Thus, the developer in such systems has the choice to inject in shallow ground water aquifers, if the geothermal fluid is environmentally benign and could also inject deeper within the fault zone, in order to be heated up before mixed again with the production line. Finally, in the case of environmentally benign fluid, the latter can be discharged on the surface.

Cooling provided by injection, seems to be the most common problem in the geothermal industry. According to Sanya et al., there are two causes for injection- induced cooling: a) Very close distance between production and injection wells, b) ‘’Short- circuiting’’ of the injected fluid to the production wells caused by a fault or fractured zone. However, the cooling problem can be identified through tracer test program conduction and could give alert to the developer.

A potential groundwater contamination can be caused by the injection of the geothermal waste on the geothermal reservoir; the main factors are the up flow of the injected water to the groundwater aquifer through a fault and the potential leakage of the injected fluid behind the casing caused by poor cement bond or probable damage due to corrosion or mechanical causes. However, through a careful geologic modeling the first cause can be avoided by locating injection wells in alternative sites.

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Leakage of injection waste water to the surface can be indentified in very shallow geothermal reservoirs (a few hundred meters). In order to avoid this kind of problem, injection should be deeper than the production level. Moreover, the occurrence of micro earthquakes near injection sites could be induced due to high pressure injection. More specifically, if the fluid pressure is increased beyond the original pore pressure and subsurface zones of weakness or active faults exist near the injection area, seismic activity may be induced. Thus, in order to avoid seismic activity, injections wells should be located away from known active faults, and the injection pressure should be lower than the original pore pressure of the system. [9]

2.3 Chemical pollution induced

Chemical pollution occurs both from gaseous components in steam that are discharged into the atmosphere and from aqueous components in spent water that may mix surface and ground waters, characterized as the most adverse environmental effect of geothermal energy utilization. Geothermal fluid may be including CH_4, CO_2, B and H_2S. The last noxious gas has an unpleasant smell when present in low and harmless concentrations. In order to reduce chemical pollution both waste water and the steam condensate should be injected into drill holes. [8]

3. THE USE OF RISK ANALYSIS

3.1 General

What is risk analysis? Risk Analysis stemmed from the Major industrial accidents of the last decades involving dangerous chemicals that pose a significant threat to humans and the environment. It involves hazard identification, hazard evaluation, the development of potential risk reducing measures, and the communication of risk information to decision makers [10].

3.2 Methods used

Risk analysis typically involves the following key steps:

- Hazard identification (HAZID)
- Frequency analysis
- Consequence analysis
- Quantification of risks using output from frequency and consequence analysis
- Investigation of potential risk reducing measures
- Development of recommendations

The common methods used in Risk Analysis are a) the hazard and Operability Analysis (HAZOP), b) the Failure Modes and Effects Analysis (FMEA), c) the “What if” scenarios, d)the Fault Tree (FT) Analysis, e) the Event Tree (ET) Analysis, f) the Risk Matrix and many other methodologies, which range from purely Qualitative to totally Quantitative and a mix of the two that are applied according to the needs and resources of the plant to be analyzed. The methods that have been used in this context are the more Qualitative ones, as the detailed engineering of each reinjection method has not yet been established.

4. CONCLUSIONS

In this study, environmental threats on geothermal power systems caused by injection of geothermal fluid were determined. Geothermal fluid injection is site specific; in some cases the impact of waste water injection is significant, but alternative solutions can be implemented in order to minimize impact and make the geothermal energy developments environmentally and economically competitive against the conventional fossil fuels systems.

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Furthermore, geothermal fluid injection, condensate as a solution to environment impacts but also helps maintaining reservoirs pressures, increasing both the operational lifetime of the production well and the reservoir lifetime. Waste fluid injection is favorable against surface disposal of waste water due to its constituents which may cause adverse effect on the environment. A safety analysis determining potential accidents in the storage phase of high enthalpy geothermal fluid has been contacted. The final conclusion is that a reinjection plan should be developed as early as possible in any conceptual study of a geothermal development taking into account that the field characteristics namely, where to inject and how deep, what reservoir fluid cooling method to use and which waste water chemistry and appropriate remediation actions to take in order to prevent scaling in injection wells.

References

[1] deLIano-Paz, F. Silvosa, A.C. Antelo, S.A. Soares, I. (2015). The European low-carbon mix for 2030:The role of renewable energy sources in an environmentally and sociall efficient approach: *Renewable and Sustainable Energy Review;* 48, pp. 49-61.

[2] Dincer, I. (2000).Renewable energy and sustainable development: a crucial review: *Renewable and Sustainable Energy Reviews;* **4**(2), pp. 157–75.

[3] Harvey, C.C. White, B.R. Lawless, J.V. Dunstall, M.G. 2010. *2005–2010 New Zealand country update*, world geothermal congress. Indonesia: pp 25–30.

[4] Bertani, R. 2015. Geothermal Power Generation in the World 2010-2014 Update Report: *Proceeding World Geothermal Congress 2015,* Melbourne, Australia, April 19-24, 2015.

[5] Andritsos N., Dalambakis P., Arvanitis A., Papachristou M. and Fytikas M. 2015. Geothermal developments in Greece – Country- update 2010-2014: *Proceedings World Geothermal Congress 2015*, Melbourne, Australia, April 19-24, 2015.

[6] Einarsson, S. S., Vides, R. a., Cuellar, G. 1975. Disposal of geothermal waste water by reinjection: *Proceeding Second United Nations Symposium on the Development and Use of Geothermal Resources,* San Francisco, 20-29 May, 1975, pp 1349-1363.

[7] Kaya,E. Zarrouk, S.J. O'sullivan, M.J. (2011). Reinjection in geothermal fields:A review of worldwide experience: *Renewable and Sustainable Energy Review; 15*, pp. 47-68.

[8] Arnorsson, S. 2004. Environmental impact of geothermal energy utilization. Ageovhemical perspective: *Energy, Waste and the Environment*; 236, pp. 297-336.

[9] Sanyal, S. K. Granados, E. E. Menzies, A.J. (1995). Injection- related problems encountered in geothermal projects and teir mitigation: the United State experience: *Proceeding of the World Geothermal Congress;* Florence, Italy, 3, pp 2019-2022.

[10] Papazoglou I. A., Nivolianitou Z., Aneziris O., Christou M. (1992). "Probabilistic safety analysis in chemical installations", *Journal of Loss Prevention in the Process Industries*, Volume 5, No 3, pp. 181-191.

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A dynamic risk and mass depletion assessment using system dynamics

A. Kalomoiri[1*], A. Koutsospyros[2], W. Braida[1]

[1] Department of Civil Environmental and Ocean Engineering, Stevens Institute of Technology, Hoboken, NJ, USA.
[2] Department of Civil and Environmental Engineering, University of New Haven, West Haven, CT, USA.
*Corresponding author: Email: akalomoi@stevens.edu

Abstract

This paper describes the development of a system dynamics framework toward a dynamic risk assessment while taking into consideration the mass depletion processes in a natural attenuated environment. The development of this framework, assumes that natural attenuation is a complex system that evolves over time. Through the cause and effects loops, this deterministic frameword, relates the contaminants mass depletion processes, physical and biological, with the different potential risk, water ingestion and air inhalation. In order to test the proposed framework, a conceptual model of a leaking Underground Storage Tank containing pure benzene in a vadoze zone has been analyzed. Geological site specifications and chemical characteristics of benzenes are considered along with fate and transport mechanisms that contribute source mass depletion, including volatilization, biodegradation, and groundwater recharge due to water infiltration processes.

Keywords: UST; system dynamics, total cancer risk, MNA; mass depletion

1. INTRODUCTION

According to the latest reports by the U.S. Environmental Protection Agency, approximately 51 percent of the total U.S. population lives within three miles of a Superfund site [1]. Those sites pose high risks on human health and the environment. Many environmental health studies suggest that a variety of human health problems including cancer [2, 3], correlate strongly with the exposure of the local community to contaminated sites through a variety of pathways, such as air inhalation, water and food ingestion, or direct contact.

Increased public awareness and concerns about the hazardous waste sites and their adverse effects on human health and the environment started to arise since the late of 1970s [4]. Remedial actions are often undertaken in order to mitigate the adverse effects of contamination. Traditionally, the objectives of the remediation actions have focused on mass reduction of contaminants of concern (COC's) using cost effective treatment methods to protect human health and the environment [4, 5]. The intensity of the risk is highly depended on the COCs fate characteristics and transport processes that evolve over time depending on the changes in weather conditions [6, 8]. This dynamic behavior needs to be taken into account in the decision making process, in order to give better estimations for the potential risks.

2. ANALYSIS

The system dynamic model (SD) developed under the systems thinking principles, using the software Vensim [10]. Systems thinking provides a better insight into a the system's behaviour while using the stock and flow structures (Figure 1) time delays and nonlinearities, determine the

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dynamic behavior of a system [2, 11, 12]. Moreover, the behavior of systems and the impact of different policies can be determined utilizing simulations.

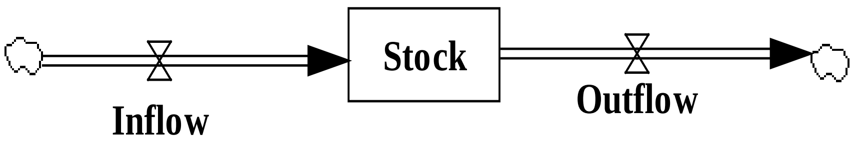


Figure 1: Stock and flow model [2].

The developed dynamic model that integrates mass depletion due to natural attenuation processes (volatilization, biodegradation, and groundwater recharge due to water infiltration processes) and assesses the receptors cancer risk via different pathways is presented in Figure 2.

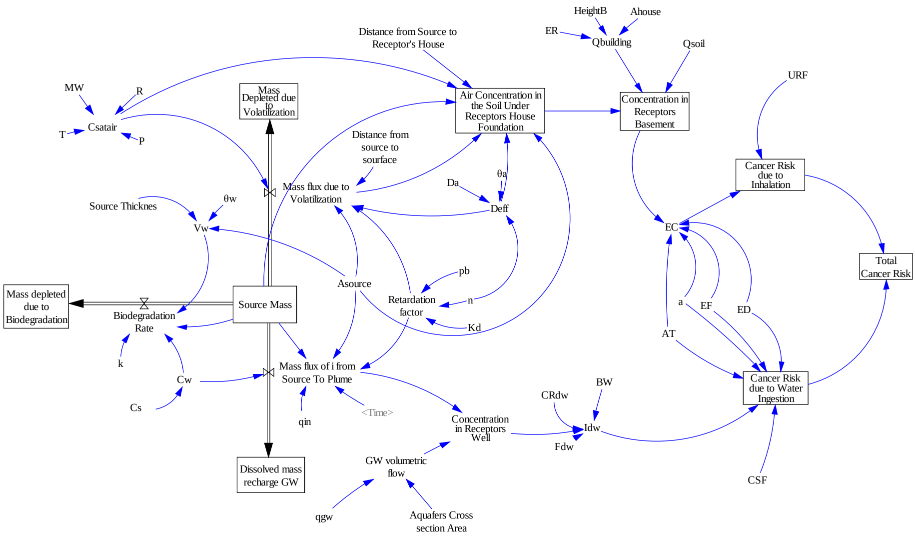


Figure 2: MNA and Risk assesment systems dynamics model [9]

The above model, is based on an assumed case study scenario which is described in more detail in the following section.

Case study

The SD model can analyze simultaneously the fate and transport of light non-aqueous phase liquid (LNAPL) mixture such are petroleum fuels. However, for simplicity, this case study considers a pure compound (benzene) in order to establish a conceptual model. In this respect, the hypothetical conceptual model illustrated in the following figure, consists of a pure compound (benzene) which is released to the environment from an underground storage tank (UST). The mass of the benzene at t_o=0 (initial conditions), is assumed to be 160 kg. The average thickness of benzene layer is 0.40m and it expands in an area of 90m^2. Benzene is released in in the vadose zone which is assumed to be homogenous with an average porosity of 0.35. The unconfined aquifer is located 10m below the spill area and the direction of the groundwater flow is toward the location of the receptor's well. The area is assumed to be a homogeneous soil with no impermeable materials present. As a result the aquifer is directly influenced by the climatic factors (precipitation, temperature) and human interventions as is irrigation.

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Depending upon the fate of the LNAPL, several receptors exposure mechanisms may be present in contamination scenarios like the one described in this paper: [7, 8]:

a) Through Surface water exposure due to recharge of surface streams
b) Through inhalation due to vapor intrusion in basements
c) Through dissolved species in groundwater via contaminated wells

In this case study, it is assumed that the receptor is exposed to benzene by two different pathways:

- Through the groundwater ingestion that is utilized from a well installed near the receptor's house and contains dissolved benzene, and
- Through the inhalation of the benzene vapor that intrudes into the house from the subsurface.

The distance between the contaminated subsurface area and the receptor's house is assumed to be 14m (X_R) and the distance to the surface area is 10m (L_R).

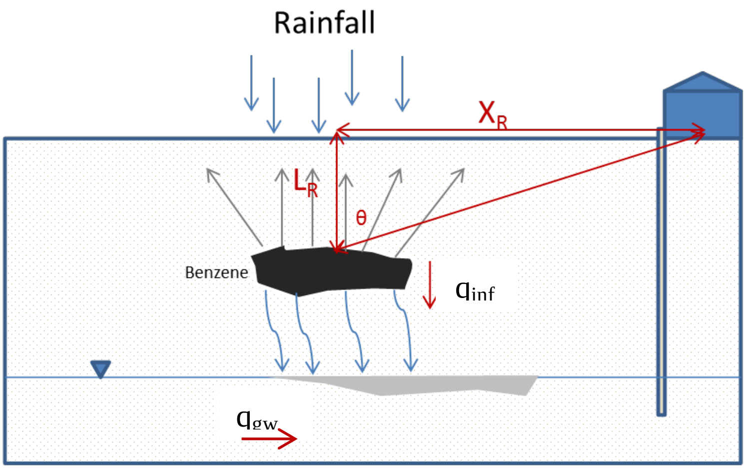


Figure 3: Conceptual model of contaminant transport and transport mechanisms (X_R = horizontal distance between plume and receptors house, LR = vertical distance between plume and surface, q_{inf} = Infiltration flow rate, q_{gw} = groundwater flow rate

The LNAPL substances, in the vadose zone, can partition into the dissolved, sorved and vapor phases depending upon composition characteristics. Partitioning, depends on the substances water solubility, soild organic carbon partition coefficient, soild organic carbon content, and volatility. After a volume of LNAPL is released, there are different transport mechanisms that contribute toward the mass depletion of the contaminants.

Specifically in this case study, the following mass fluxes are recognized:

- A gaseous mass flux which occurs by direct volatilization of LNAPL (benzene) into the gas phase, following Henry's law,
- A dissolved mass flux which is the result of water infiltration in the vadose due to weather processes (precipitation), or human interventions (irrigation).

In addition, two transformation-transport mechanisms contribute to contaminant mass depletion and are taken into consideration in this exercise:

- Biodegradation which plays an important role toward LNAPLs mass depletion,
- Sorption-desorption quantified by the retardation factor which evaluates transport delays.

System dynamics allows incorporation of other environmental parameters, such as temperature, pH etc., and their changes over time, however, for simplicity reasons they are not considered in this exercise.

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Governing Equations

The equations used in the model both for mass depletion and risk assessment are presented in Tables 1-3.

Table 7. Cancer risk equations due to vapor inhalation and water ingestion [13, 14]

Cancer risk equations
Cancer risk due to vapor inhalation $CR_{inh}^{i} = EC \times URF^{i}$
Exposure concentration $EC = \frac{C_a \times EF \times ED}{AT \times 365 days / year}$
Cancer risk due to water ingestion $CR_{ing}^{i} = \frac{I_{gw} \times EF \times ED \times CSF}{AT \times 365 days / year}$

Table 2: Values used to estimate the cancer risk due to benzene vapor inhalation

List of Symbols		**Values**	**Units**
CR_{dw}	Drinking water rate consumption	0.67	l/d
F_{dw}	Fraction of drinking water contaminated	1	-
BW	Body weight	15	kg
EF	Exposure frequency	29	d/mo
ED	Exposure direction (highest)	6	years
CSF	Cancer slope factor	2.7×10^{-3}	kg·d/gr
AT	Averaging time	70	yr
URF^{i}	Inhalation unit risk factor	7.8×10^{-6}	g/cm^3

Table 3: Equations for estimating mass depletion through natural attenuation processes [7]

Mass depletion equations		
Volatilization	Dissolved mass flux to groundwater recharge from	Biodegradation
$J_{vol}^{i} = C_{air,i}^{sat} \frac{D_{eff}^{i}}{z} H_s \times L_s$	$J_{in}^{i} = C_{w,i}^{sat} \left(1 - e^{-\frac{t}{\tau}}\right) A_s \times q_{in} \times f$	$J_b = C_{w,i}^{sat} \times k \times V_w$
$D_{eff}^{i} = D_a \times \frac{\theta_a^{3.33}}{n^2}$	$\tau = \frac{V_s}{q_{in} \times A_s}$	$V_w = \theta_w \times A_s \times T_s$
$C_{air,i}^{sat} = x_i \frac{P_i \times MW_i}{R \times T}$	$C_{w,i}^{sat} = x_i \times C_s$	

The retardation factor is given by the equation:

$$R = 1 + \frac{\rho_b}{n} \times K_d , \qquad [1]$$

The values that have been used in order to run the simulations for this exercise are given in Table 4.

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Table 4: Values used to estimate the cancer risk due to benzene vapor inhalation

List of Symbols		Values	Units
A_s	Source area	9×10^5	cm^2
C_s	Water solubility	1.7×10^{-3}	gr/cm^3
D_a	Free air diffusivity	2.44×10^4	$cm^2/month$
K_d	Distribution coefficient	0.01178	cm^3/gr
K	Rate constant	1.05	$month^{-1}$
MW_i	Molar mass	78.11	gr/mole
N	Porosity	0.35	-
P_i	Benzene vapor pressure	12.7	kPa
q_{in}	Infiltration rate	9	cm/month
T_s	Source thickness	40	cm
T	Absolute temperature	297	K^0
x_i	Mole fraction	1	-
L_R	Source to surface distance	1000	cm
θ_w	Water field porosity	0.07	-
θ_a	Air field porosity	0.28	-
ρ_b	Soils bulk density	1.65	gr/cm^3

3. RESULTS / CONCLUSSIONS

Considering that all the processes evolve through time the system's dynamics model simulation computes mass depletion and carcinogenic risk assessment over time, as shown in Figures 4 and 5, respectively.

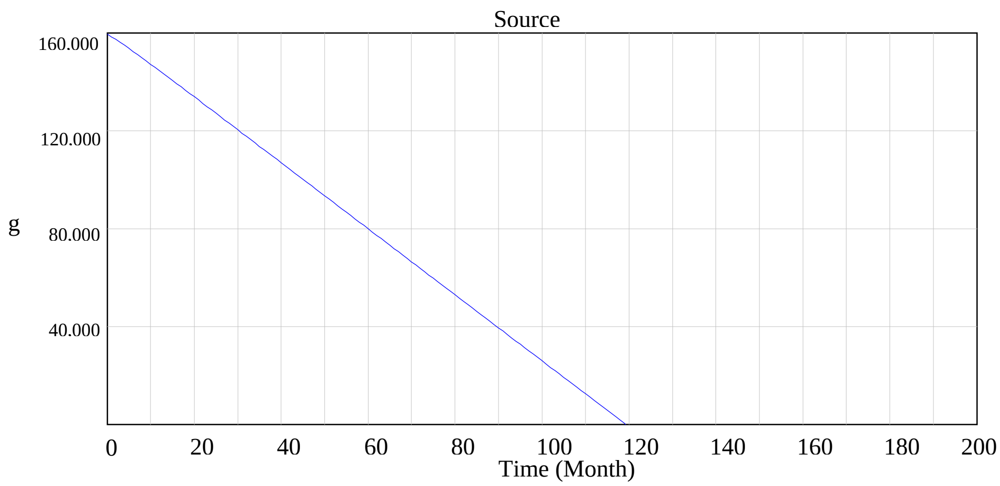


Figure 4: Benzene mass depletion.

Figure 4 shows that benzene mass is taking approximately ten years to deplete. That mass depletion is site specific, as it considers specific weather and geological characteristics which influence the infiltration rate, and how each of the transport and transformation processes mentioned above evolve over time.

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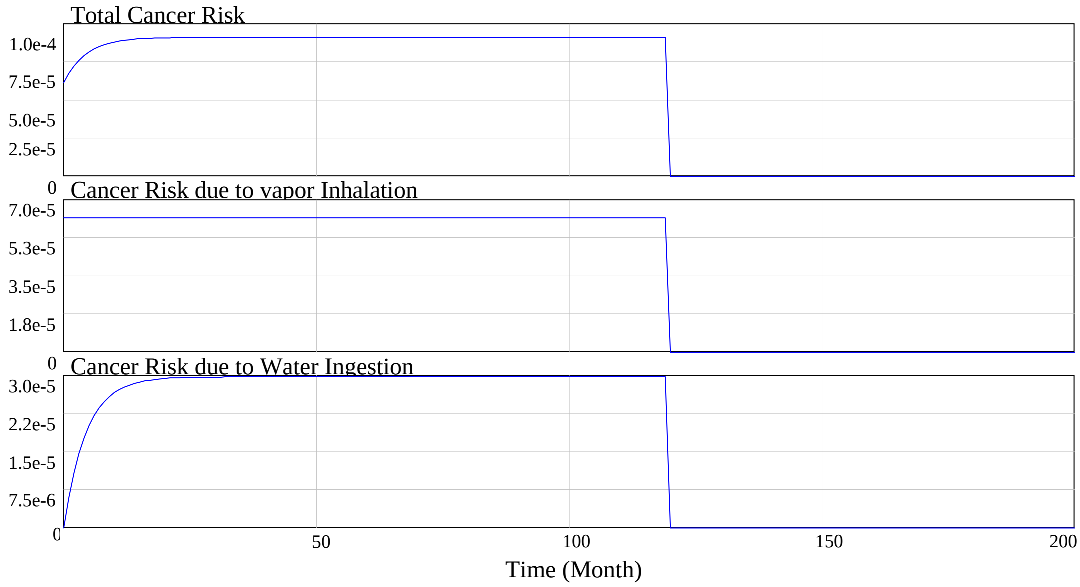


Figure 5: Total cancer risk, and risks associated to vapor inhalation and water ingestion

Figure 5, shows that the cancer risks associated with two distinct exposure routes, namely, vapor inhalation and water ingestion are above the benzene threshold risk. According to the *Guidelines for carcinogen risk assessment*, the threshold risk of benzene is 10^{-6} which indicates the risk of 1:1,000,000 risk of cancer. The total carcinogenic risk is derived from the summation of the risk for each of the exposure pathways (inhalation and water ingestion considered in this study). As shown in Figure 5, the total carcinogenic risk is greater than 10^{-4} and exceeds the threshold by two orders of magnitude. Therefore, in order to mitigate the receptor's potential adverse health risk, remediation actions are necessary.

Moreover, Figure 5 shows that the receptor is rapidly affected by the contaminated air and the risk due to air inhalation reaches a maximum value of $6.8x10^{-5}$ instantaneously and remains constant thereof. This can be explained by the constant air field porosity assumption for the specific system boundaries. On the other hand, the cancer risk due to water ingestion attains the maximum value of $3x10^{-6}$ in approximately 25 months. This can be explained by the transient nature of the water infiltration which takes time to become established in the vadose zone. Once the contaminated plume fills the pore spaces, it will constantly supply (under a constant q_{inf}) the groundwater system with dissolved benzene and eventually reaches the receptor's well, posing a cancer risk due to water ingestion.

As a result of this analysis, we can conclude that system dynamics can provide a better estimation of the overall risk in which a receptor is exposed, even in the initial stages of investigation where the information is limited [9]. It is important to know the potential pathways by which the COC reaches the receptor as well as the associated risk of exposure in order to avoid adverse health effects. This can provide a better strategy in terms of risk mitigation and mass depletion, as for example, in this case study, a ventilation system could be installed in receptors home in order to mitigate the risk due to air inhalation, while simultaneously, the receptor should be advised to stop using the water for ingestion purposes. This serves the following two purposes: a) it reduces the receptor's risk before the remediation actions start to implement and b) at the same time, the system can attenuate the COCs.

Evidently system dynamics can be an effective tool in the hands of engineers that can help optimize remediation schemes while at the same time considering exposure risks associated with the various remedial methods.

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REFERENCES

[1] http://www.epa.gov/sites/production/files/2015-09/documents/oswer_tribal_accomplishments_report_2013_508.pdf (accessed March 6, 2015).

[2] Sterman, J., 2000. *Business dynamics: Systems thinking and modeling for a complex world*. Boston: Irwin/McGraw-Hill.

[3] U.S EPA. 1987. *Superfund public health evaluation manual*. Washington, D.C.: Office of Emergency and Remedial Response.

[4] Havranek, T., 1999 Modern project management techniques for the environmental remediation industry. St. Lucie Press.

[5] http://www.bespacific.com/46976-2/ (accessed January 18, 2015).

[6] Corbitt, R. A., 1990. *Standard handbook of environmental engineering*. New York: McGraw-Hill.

[7] Huntley, D., & Beckett, G., 2002. Persistence of LNAPL sources: Relationship between risk reduction and LNAPL recovery. Journal of Contaminant Hydrology, 59(1-2), 3-26.

[8] Fetter, C., 1993. *Contaminant hydrogeology*. New York: Macmillan Pub.

[9] Kalomoiri, A., 2016. Promoting sustainable remediation decisions, through a dynamic lifecycle, and risk assessment model (Unpublished Doctoral dissertation). Stevens Institute of technology, Hoboken, NJ, 07030 ProQuest Dissertations and Theses. (Accession Order No: pending)

[10] http://vensim.com/ (accessed March, 2012).

[11] Chang, N., 2011. *Systems analysis for sustainable engineering: Theory and applications*. New York: McGraw-Hill. *Contaminants in the subsurface source zone assessment and remediation*. (2005). Washington, DC: National Academies Press.

[12] Bossel, H., 2007. *Systems and models: Complexity, dynamics, evolution, sustainability*. Norderstedt: Books on Demand.

[13] U.S EPA., 2005. *Guidelines for carcinogen risk assessment*. Washington, D.C.: Risk Assessment Forum, U.S. Environmental Protection Agency.

[14] Theodore, L., & Dupont, R. R., 2012. *Environmental health and hazard risk assessment: Principles and calculations*. Boca Raton: CRC Press.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
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Discrimination of lithogenic and anthropogenic sources of metals in soils developed on ultramafic bedrock

D. G. Megadouka[1], D. L. Bouranis[2], K. G. Serelis[1*]

[1] Department of Natural Resources Management & Agricultural Engineering,
Agricultural University of Athens, 118 55, Athens, Greece.
[2] Department of Crop Science, Agricultural University of Athens, 11855, Athens, Greece.
*Corresponding author: Email: serelis@aua.gr

Abstract

To determine the speciation and to identify the origin of the heavy metals Ni, Cr, Co, Pb, Zn and Cd in soils of north Evia, Greece, samples were collected from topsoil and subsoil of 21 sampling sites. Metal fractionation was obtained following a 4-step sequential extraction scheme and the following fractions were collected for each sample: the acid soluble (1st), the reducible (2nd), the oxidisable (3rd), and the residual (4th) one. High concentrations of Ni (mean 2542mg kg^{-1}) Cr (mean 606mg kg^{-1}) and Co (mean 118mg kg^{-1}) were found due to ultramafic parent rocks. Cr, Ni and Zn were associated with the 4th fraction (~82%, ~66%, ~72% respectively). Co and Pb were associated with non-residual fraction, while Cd presented different associations at each depth. Cluster analysis identified 2 main clusters: one that includes Co, Ni, Cr and Zn and represents the natural geochemical associations and another that represent anthropogenic sources (e.g. vehicle emissions, fertilizers).

Keywords: geogenic contamination; heavy metals; soil fractionation; North Evia

1. INTRODUCTION

Potentially Toxic Elements (PTE) are naturally present in soils as a result of weathering of PTE rich parent materials (e.g. geochemical anomalies in mining or volcanic contexts). Lithogenic PTE are considered being less mobile than those of anthropogenic origin [1,2]. The parent material largely influences heavy metal content in many soil types, with concentration sometimes exceeding the critical values [3,4]. Chromium and nickel are present in high concentrations in soils developed on ultramafic rocks; up to 125,000 mg kg^{-1} of Cr [5] and more than 10.000 mg kg^{-1} of Ni [6,7] were observed, while the concentrations of these metals in other soils commonly range from 0 to 100 mg kg^{-1} [8,9].

Potential risk for the environment is not determined by the PTE total concentration. Heavy metal availability depends on their origin [8], their distribution among the soil constituents, and edaphic properties, such as pH, Eh, clay and organic matter contents [10]. Knowledge of the PTE solid speciation, corresponding to their chemical binding forms, gives more useful information about PTE mobility, bioavailability and potential toxicity [11]. Sequential extraction procedure is frequently employed in order to determine the PTE speciation in natural soils and sediments as well as in materials of industrial origin [12,13,14,15].

The objective of this study was to analyze the geo-chemical behavior of six metals (Ni, Co, Cr, Zn, Cd, Pb) present in soils produced by mafic and ultramafic rocks of north Evia, and to investigate the origin of elevated trace metal concentrations observed. To accomplish this goal, the trace metal concentrations were determined, using the modified BCR sequential extraction method.

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C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
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2. MATERIALS AND METHODS

2.1 Study area and sampling

The study area is located at the north part of Evia island, Greece. This area was selected due to its parent rock. Geologically, north Evia is covered by mafic and ultramafic rocks, i.e. dunites, serpentinized peridotites, harzburgites, lherzolites [16,17,18]. These types of rocks are known to have a chemical composition characterized by high content of heavy metals, such as Ni and Cr, which are accumulated during the weathering processes in the soil [19].

Soil samples from 21 sites of north Evia (Figure 1) were taken from two depths: 0 - 10 cm (topsoil; A) and 10 - 30 cm (subsoil; B). In the laboratory, all samples were air dried and sieved to pass through a 2mm mesh.

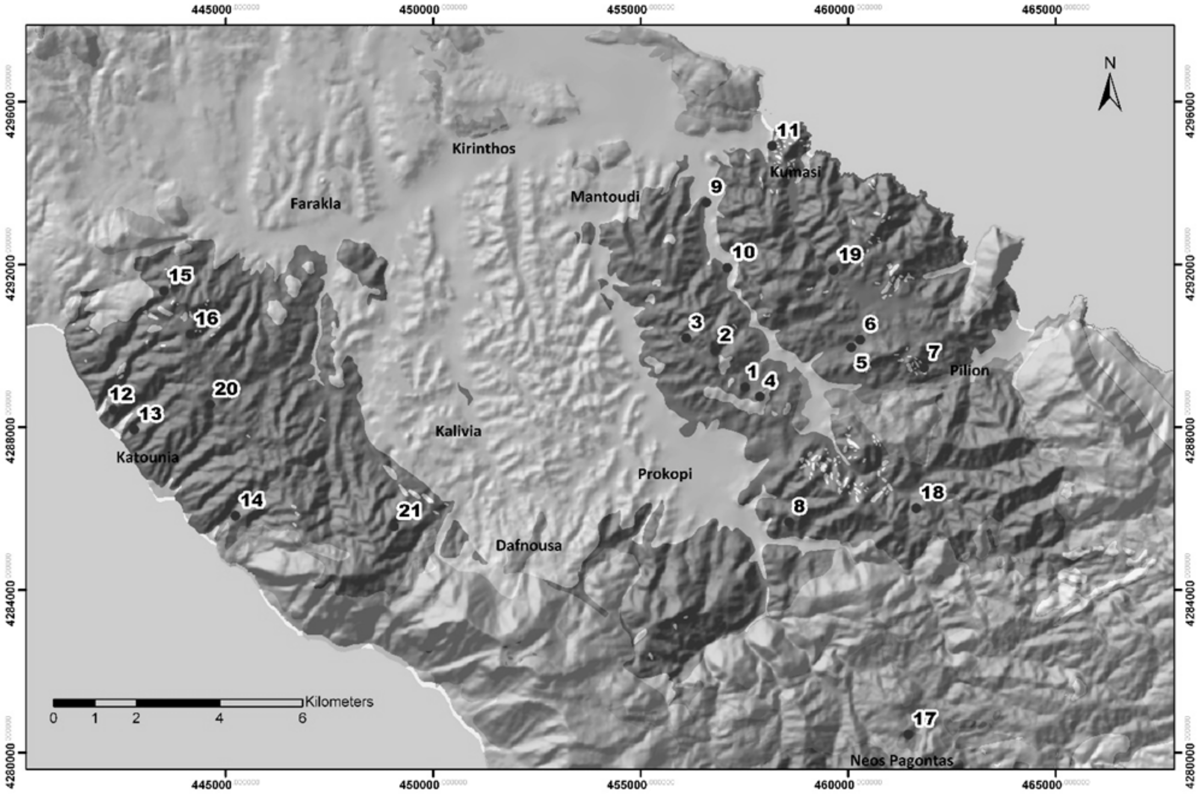


Figure 1. Location of sampling points on north Evia.

2.2 Analytical methods

The physicochemical properties of the soil samples were determined by means of standard methods. PH and Eh were determined in a ratio 1:1 soil/distilled water, organic matter content by the Walkley–Black method, $CaCO_3$ content using a Bernard calcimeter [20] while particle-size distribution was based on Stokes' Law standard procedure. For the fractionation of heavy metals an optimised BCR procedure was followed (Table 1) [21]. Each extraction step was performed in triplicate, starting with 1 g of sample. All reagents were of analytical grade quality. Concentrations were determined using Atomic Absorption Spectroscopy.

2.3 Statistical analyses

Hierarchical Cluster Analysis (HCA) is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behavior of dataset without making a priori assumption about the data, to classify the objects of the system into clusters based on their nearness or similarity [22]. HCA classifies a set of observations into two or more mutually exclusive unknown groups based on combination of internal variables. HCA was applied using Ward’s algorithmic method of

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agglomeration and squared Euclidean distance as the measurement of similarity. Results are presented in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters are represented [23]. Statistical analyses were applied using SPSS 11.0 statistical computer program.HCA has been used to classify the heavy metals and help identify the sources, whether anthropogenic or natural [24,25,26].

Table 1. Reagents and conditions employed for the modified BCR sequential extraction procedure

Step	Fraction	Reagent & conditions
1	Acid extractable	1 g of air-dried soil + 40mL 0.11 mol L^{-1} CH_3COOH, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. The residue was washed by adding 20 ml of distilled water, shaken for 15 min & centrifuged for 20 min at 3000 rpm.
2	Reducible	Residue + 40mL 0.5 mol L^{-1} NH_2OH-HCl, pH=1.5, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. Residue washing as in step 1.
3	Oxidisable	Residue digested with 10mL 8.8 mol L^{-1} H_2O_2, 1 h at room temperature, 1 h at 85 ^oC in a water bath and reduced to 2-3 mL. Then 10 mL 8.8 mol L^{-1} H_2O_2 added, 1 h at 85 ^oC in a water bath and reduced to 2-3 mL, 50 mL of 1 mol L^{-1} NH_4COOCH_3 was further added, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. Residue washing as in step 1.
4	Residual	Residue + 7 mL 12 mol L^{-1} HCl, 2.3 mL 16 mol L^{-1} HNO_3, 16 h at room temperature, 2 h gentle reflux, cool, filtered through Whatman 540.

3. RESULTS AND DISCUSSION

3.1 Soil properties

Thirteen samples out of 21 of depth A presented pH values ranging between 6.6 - 7.1, thus reflecting neutral conditions. Eh ranged from 220 – 295 mV, suggesting aerobic conditions, where the metals are usually in the form of cations. Organic matter content ranged from 0.8-13.1%, while $CaCO_3$ content ranged from 3.4 -16.6%. The majority of samples at depth A presented sandy-clay-loam and clay-loam soil texture. Regarding physicochemical properties of depth B, pH ranged from 6.4-7.8 with 14 samples being characterized by neutral conditions. Eh conditions were the same as those of depth A (227 – 298 mV) and organic matter ranged from 0.9-5.6%. $CaCO_3$ content ranged from 4.9 – 13.8%. The majority of the samples at depth B presented also sandy-clay-loam and clay-loam soil texture.

3.2 Geochemical forms of metals in soil

Ni – At depth A, the majority of the Ni was mainly in the residual fraction (65% of the total), while Ni also absorbed at reducible fraction reached 20% of the total. Ni concentrations at oxidisable fraction reached 11% and the acid extractable had much lower values up to 4%. Similar metal distribution was found at depth B at four fractions (4th: 66%, 2nd: 20%, 3rd: 10% 1st: 4%), which probably indicate that the presence and distribution of Ni at both depths is influenced by the same factors. Regarding total Ni concentrations for depth A the range was 71.1 - 4043.5 mg kg^{-1} and for depth B 92.1 - 4155.3 mg kg^{-1}. According to Selinus et al., [27] the maximum permitted level for Ni is 30-75 mg kg^{-1}. The above number was exceed up to fifty times in the studied soil samples, as expected since Ni is present at high concentrations in soils developed on ultramafic rocks more than 10.000 mg/kg^{-1}[28].

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Cr – A significant fraction of Cr was linked to the residual soil fraction, reaching 82% of the total at both depths. The oxidizable fraction had absorbed the 16% and 15% of the total Cr at depths A and B respectively, while the reducible and acid extractable fraction had negligible values reaching 1-2% of the total. The high values of Cr at residual fraction indicate its natural origin at the study area. Kierczak et al. [29] suggested that Cr associated at residual fraction (>76%) at soils has been derived from serpentinized rocks, while mineralogical analyses before extraction have shown that Cr is associated with highly resistant spinels (Cr-magnetite) which are known to dissolve during the last step of extraction.

Co –The reducible fraction corresponded to the highest Co levels obtained, ranging from 69% at depth A to 72% at depth B. Co absorbed at residual fraction was 16% at both depths, while at oxidisable fraction were 10% and 9% at each depth. Concentrations at acid extractable fraction were very low, with many soil samples having no-detectable (ND) amounts extracted reached 6% and 2% respectively. Co is typically found at higher concentrations in ultrabasic rocks, where it is associated with olivine minerals, consequently soil developed from ultrabasic rocks is usually enriched with Co [30]. During weathering processes, Co is relatively easily mobilized and the resulting distribution in soils depends on clay content and the distribution of Fe and Mn oxides [31]. Total concentrations for Co at depth A ranged from 28.2 – 191.6 mg kg^{-1} and for depth B 54.7 - 229.5mg kg^{-1}.

Zn – Zn was mostly held in the residual fraction (70% and 73% at each depth) in all samples. At reducible fraction, Zn amount extracted reached 20% and 17% of the total, respectively. Lower concentrations found at oxidisable fraction reaching 7% and 9%, while at acid extractable the values were insignificant (3% and 1%, respectively). According to Selinus et al., [27] the maximum permitted level for Zn is 150 - 300 mg kg^{-1}. In this survey, any soil sample was above this limit. In particular, total concentrations at depth A ranged from 42.6-75.0 mg kg^{-1} and at depth B from 31.8-76 mg kg^{-1}. Zinc occurs in natural soils as a result of weathering of the soil parent material, and total Zn contents in soils in average ranges from 40 to 120 mg kg^{-1} depending on their lithology [32].

Cd – Cd concentrations in the study area showed no homogeneity among soil samples and no covariance between the two depths. At depth A, Cd dominates at acid extractable fraction with 33% of the total, followed by the reducible fraction (24%). Oxidisable and residual fractions reaches 20% and 23% of the total Cd, respectively. However, at depth B, Cd dominates at residual fraction with 47%, while acid extractable and reducible fraction extracted 22% each. The concentrations at oxidisable fraction were negligible, except of three soil samples, and thus reached 9% of the total Cd. Total concentrations of Cd at depth A ranged from ND – 6.2 mg kg^{-1} and at depth B from ND – 4.7 mg kg^{-1}.The main minerals in igneous rocks, which have been reported to contain significant amounts of Cd, are biotite (4.8 mg kg^{-1}) [33] and riebeckite (5.8 mg kg^{-1}) [34]. Moreover it should be mentioned, that since 1969 mines of ferronickel ores operate at central Evia and the slag as a by-product of nickel production contains heavy metals including Cd. So the presence of Cd in the study area maybe is related both to natural and anthropogenic sources.

Pb – Pb at depth A was associated with acid extractable fraction with 44% of the total, followed by the oxidisable fraction with 27%. Regarding reducible and residual fraction, Pb extracted at 14% and 10% respectively. At depth B, Pb was mostly related with the oxidisable fraction at 39% and with acid extractable fraction at 35%. Reducible and residual fraction presented lower values reaching 6% each. According to Selinus et al., [27] the maximum permitted level for Pb is 50-300 mg kg^{-1}. In the present study, all soil samples had much lower concentrations than the above limit, ranging from ND to 122.8 mg kg^{-1} in depth A and from ND to 83.5 mg kg^{-1} in depth B. Probably the limited presence of Pb in the studied soils is due to the deposition of particles from vehicle emissions. Such emissions enrich the air and areas by roadways [35], 10% of which settle out in 100m of the roadway, 45% within 20km, 10% within 20-200km and 35% is carried on long-range atmospheric transport systems [36].

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Table 2. Metal concentrations (mg kg^{-1}) in each fraction of modified BCR in soil samples at two depths. A: topsoil, B: subsoil, ND: not detected.

	Acid extractable	Reducible	Oxidisable	Residual
NiA	0 – 142.6	4.08 – 1033.6	21.8 – 1018	30.5 – 2244
NiB	17.4 – 135.9	ND – 1238.4	68.4 – 391.9	26.3 – 2624.1
CrA	ND – 3.8	ND – 38.8	ND – 169.7	39.3 – 2401.2
CrB	ND – 29.8	ND – 40.8	ND – 176.5	12.4 – 2082.6
CoA	ND – 23.4	21.6 – 135.6	ND – 48.3	ND – 50.6
CoB	ND – 15.8	37.4 – 144.9	ND – 42.8	ND – 64.1
ZnA	ND – 4.9	3.5 – 20.4	1.9 – 8.1	28.5 – 54.0
ZnB	ND – 3.4	3.9 – 25.2	0.7 – 26.5	22.0 – 53.7
CdA	ND - 3.3	ND –3.3	ND – 1.6	ND – 2.6
CdB	ND – 3.0	ND – 2.6	ND – 1.3	ND – 3.0
PbA	ND – 36.0	ND – 32.0	ND – 60.2	ND - 27.0
PbB	ND – 27.4	ND – 34.1	ND – 47.5	ND - 34.2

3.3 Assessment of potential environmental risk

In order to estimate the environmental risk associated with heavy metal pollution in the study area, the soil samples were classified according to a Risk Assessment Code (RAC), based on the strength of the bond between metals and the different geochemical fractions in soils and the ability of the metals to be released and enter into the food chain [37]. RAC is defined as the percentage of the ratio of the FI fraction (exchangeable and carbonate fraction) to the total concentration of elements in the soil [37] (table 3).

Table 3. The result of risk assessment code for soil samples of the study area.

	No risk <1% RAC	Low risk 1–10% RAC	Medium risk 11–30% RAC	High risk 31–50% RAC	Very high risk >50% RAC
NiA	1	19	-	-	-
NiB	-	20	-	-	-
CrA	12	7	-	-	-
CrB	11	6	2	-	-
CoA	10	6	3	-	-
CoB	14	7	-	-	-
ZnA	-	-	-	-	-
ZnB	-	-	-	-	-
CdA	-	1	3	1	2
CdB	1	1	-	1	2
PbA	-	-	-	-	-
PbB	-	-	-	-	-

3.4 Cluster analysis

Topsoil –Results revealed two main groups for soil samples at depth A (Figure 2). The first group includes two clusters between Co-Ni and Cr-Zn. The strongest correlation was obtained between Co and Ni. Thus, the first group confirms the natural origin of these four metals as it is known that they are associated with basic and ultrabasic rocks. The second cluster contained the elements Cd and Pb of anthropogenic origin, with a very weak correlation between them.

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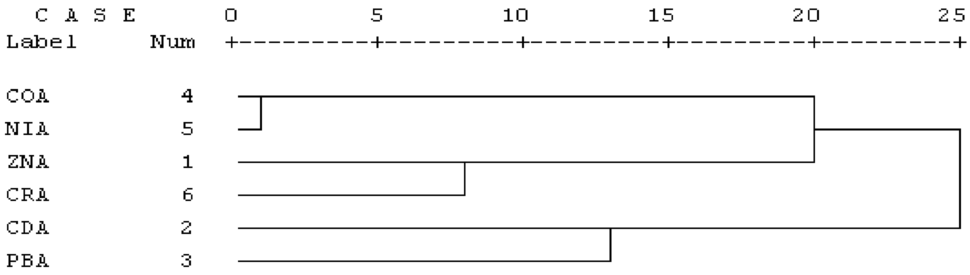


Figure 2. Dendrogram obtained by cluster analysis for heavy metal contents.

Subsoil – The same grouping was obtained from cluster analysis at depth B (Figure 3). Results revealed two clusters of elements: the first one included the same elements as depth A, previously been interpreted as elements of natural origin (Co-Ni and Zn-Cr), but also Cd. Thus, Cd at depth B associates with the metals of lithogenic origin, indicating its natural source by biotite and riebeckite of parent rocks. Also, it should be noted that the correlation between Zn-Cr at depth B was equally strong as Co-Ni. Finally, Pb was found isolated, indicating clearly its anthropogenic origin.

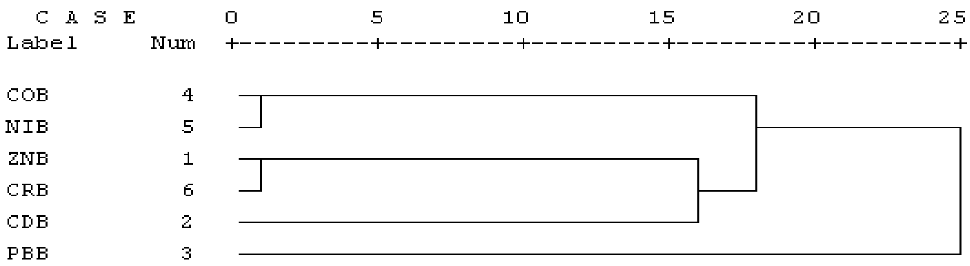


Figure 3. Dendrogram obtained by cluster analysis for heavy metal contents

4. CONCLUSIONS

The presence of Ni, Cr, Co and Zn in soils of north Evia was due to parent material of the area, which consists of mafic and ultramafic rocks. Thus, because of the weathering of the parent rock, metals are released and bind to solid phase of the soil. Ni is considered to be of low environmental risk, according to RAC. Cr although it was found at high total concentrations has also low environmental risk as also Co. The study area was not contaminated by Zn, as it was found in low concentrations. Pb in the investigated soils is considered of purely anthropogenic origin from car emissions of the road network, however the area cannot be considered contaminated by Pb. Finally, Cd seems to have both anthropogenic and natural origin and in few soils samples has moderate to very high environmental risk. The main anthropogenic sources are probably of airborne particle deposition of slag from the activities of ferronickel ores, as well as from insecticides, pesticides and phosphate fertilizers.

References

[1] Chlopecka, A., Bacon, J.R., Wilson, M.J., Kay, J., 1996. Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland. *J. Environ. Qual.* **25**, 69–79.

[2] Karczewska, A., 1996. Metal species distribution in top- and sub-soil in an area affected by copper smelter emissions. *Appl. Geochem*. **11**, 35–42.

[3] Palumbo, B., Angelone, M., Bellanca, A., 2000. Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. *Geoderma* **95** (3–4), 247–266.

ISBN: 978-960-6865-94-7

[4] Salonen, V., Korkka-Niemi, K., 2007. Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland. *Applied Geochemistry*. **22**, 906–918.
[5] Adriano, D.C., 1986. *Trace Elements in the Terrestrial Environment,* Springer Verlag, New York,.
[6] Hseu, Z.Y.,2006. Concentration and distribution of chromium and nickel fractions along a serpentinic toposequence. *Soil Sci.***171** 341–353.
[7] Oze, C. Fendorf, S. Bird, D.K. Coleman, R.G. 2004. Chromium geochemistry of serpentine soils,.*Int. Geol. Rev.* **46** 97–126.
[8] Kabata-Pendias, A. 2000. *Trace Elements in Soils and Plants*, 3rd Ed, CRC Press, Boca Raton, Florida, USA.
[9] McGrath, S.P., *Chromium and nickel*, 1995. in: B.J. Alloway (Ed.), Heavy Metals in Soils, 2nd Ed., Blackie, London, UK, pp. 152–177.
[10] McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils, *Adv. Soil Sci.* **10** 1–56.
[11] Stegmann, R., Brunner, G., Calmano, W., Matz, G., 2001. *Treatment of Contaminated Soil.* Springer, Berlin, Germany.
[12] Usero, J., Gamero, M., Morillo, J., Gracia, I., 1998. Comparative study of three sequential extraction procedures for metals in marine sediments. *Environ. Int*. **24**, 487–496.
[13] Amir, S., Hafidi, M., Merlina, G., Revel, J.-C., 2005. Sequential extraction of heavy metals during composting of sewage sludge. *Chemosphere* **59**, 801–810.
[14] Kim, B., McBride, M.B., 2006. A test of sequential extractions for determining metal speciation in sewage sludge-amended soils. *Environ. Pollut*. **144**, 475–482.
[15] Dere, C., Lamy, I., Jaulin, A., Cornu, S., 2007. Long-term fate of exogenous metals in a sandy Luvisol subjected to intensive irrigation with raw wastewater. *Environ. Pollut.* **145**, 31–40.
[16] Gartzos, E., Migiros, G., Serelis, K., Parcharidis, I., 1994. Ultramafic rocks Evia - Eastern Thessaly and Cr concentrations. *Brochures. El. Geological. Company*. Vol. XXX / 3 p.137-153.
[17] Dimakos, G., 1993. Petrography and Geochemistry of ultramafic rocks of Evia. IGME, Athens.
[18] Valeton, I., Biermann, M., Reche, R., Rosenberg, F., 1987. Genesis of nickel laterites and bauxites in Greece during the Jurassic and Cretaceous, and their relation to ultrabasic parent rocks. *Ore Geology Reviews* **2**, p.359-404.
[19] Alloway, B. J., 1995. *Heavy metals in soil* (2nd ed.). London: Blackie Academic & Professional.
[20] Allison, L.E and Moodie, C.D., 1965. *Carbonate in: Black C.A. Methods of soil analysis*, Part 2. ASA, USA.
[21] Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monitor*. **1**, 57–61.
[22] Vega, M., Pardo, R., Barrado, E., & Deban, L., 1998. Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research*, **32**, 3581–3592.
[23] Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* **65**, pp. 863–872.
[24] Lee, C.S., Li, X.D., Shi, W.Z., Cheung, S.C., Thornton, I., 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS a multivariate statistics. *Science of the Total Environment* **356**, 45–61.
[25] Li, X.P., Feng, L.N., 2012. Multivariate and geostatistical analyzes of metals in urban soil of Weinan industrial areas, Northwest of China. *Atmospheric Environment* **47**, 58–65.
[26] Wang, X.S., Sun, C., 2009. Pt and Pd concentrations and source in urban roadside soils from Xuzhou, China. *Environmental Geology* **56**, 1129–1133.
[27] Selinus O., Alloway B., Centeno J.A., Finkelman R.B., Fuge R., Lindh U. and Smedley P., 2005. *Essentials of Medical Geology – Impacts of the natural environment on public health*. Elsevier Academic Press, USA. pp. 812.
[28] Hseu, Z.Y., 2006. Concentration and distribution of chromium and nickel fractions along a serpentinic toposequence, *Soil Sci.* **171** pp.341–353.
[29] Kierczak, J., Neel, C., Aleksander-Kwaterczak, U., Helios-Rybicka, E., Bril, H., Puziewicz, J., 2008. Solid speciation and mobility of potentially toxic elements from natural and contaminated soils: A combined approach. *Chemosphere* **73**. pp. 776–784.
[30] Nagpal, N.K., 2004. *Water quality guidelines for cobalt. Ministry of Water, Land and Air Protection, Water Protection Section, Water, Air and Climate Change Branch*, Victoria.
[31] Paveley, CF., 1988. *Heavy metal sources and distribution in soils, with special reference to Wales*. Bradford UK: University of Bradford.
[32] Kabata-Pendias, A., 2001. *Trace elements in soils and plants*. New York: CRC Press LLC.
[33] Waketa, H., Schmitt, R.A., 1970. Cadmium. In: K.H. Wadepohl (Ed.), *Handbook of Geochemistry*, vol. **11-2**. Verlag, Berlin, p. 48 B.
[34] Holmes, R., 1976. *The regional distribution of cadmium in England and Wales*. Ph.D. Thesis, University of London, London, UK.

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[35] Adriano, D.C., 2001. *Trace elements in terrestrial environments* – Biochemistry, Bioavailability and risks of metals. Springer – Verlag, New York. pp. 867.
[36] OECD Organization for Economic Cooperation and Development, 1993. Risk Reduction. Monograph 1: Lead. Paris.
[37] Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. *Journal of Environmental Management* **90**, pp. 1106–1116.

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Barriers identification regarding the implementation of an environmental management system in a bakery-confectionary industry in Cyprus

I. Voukkali[1*], A. Zorpas[2], P. Loizia[1], D. M. Pociovalisteanu[3]

[1] I.E.S.T - EnviTech Ltd, (Institute of Environmental Technology and Sustainable Development, Department of Research and Development) www.envitech.org, Paralimni, Cyprus.
[2] Cyprus Open University, Faculty of Pure and Applied Sciences, Environmental Conservation and Management, Nicosia, Cyprus.
[3] ConstantinBrâncuşi" University of Târgu-Jiu, Faculty of Economics, Romania.
*Corresponding author: Email: irenevoukkali@envitech.org

Abstract

Food industry is facing increasing pressure to ensure that their activities are environmentally sensitive, but there is also increased internal pressure to maintain or increase profitability in the face of fierce competition. The main environmental issues for the food industry are water, energy and natural sources consumptions, solid and liquid waste management, chemicals, biodiversity, land use and air pollution. It is therefore necessary, each food industry to establish and implement an integrate management system to identify, manage and control those issues. An Environmental Management System (EMS) could help any organization to achieve its environmental goals through specific goals and targets in order to improved organization environmental performance. The purpose of this paper to analyze the barriers that arise during the implementation of an integrated and efficient EMS in Cyprus food industry (bakery / confectionary) in the framework of the international standard ISO 14001. The major problems arising from the implementation of the ISO 14001:2004 system were according to paragraph 4.5.3 focus on non-conformities, corrective actions and preventing actions, as well as on paragraph 4.4.6 focus on the operational control parameters

Keywords: environmental management system; ISO 14000; bakery/confectionary industry; environmental impacts

1. INTRODUCTION

Food industry is facing increasing pressure to ensure that their activities affect the environment as are considered to be sensitive, but there is also increased internal pressure to maintain or increase profitability in the face of fierce competition. The crucial environmental issues for the food industry are water, energy and natural sources consumptions, solid and liquid waste, chemicals, biodiversity, land use and air pollution [1].It is therefore necessary, each food industry to establish and implement a structured management system to identify their issues rising from their actions, take measures for limited their environmental impacts and also insurance that is performance meet its legal and policy requirements.The EMS has several Objectives, which are: (i) Encouraging SMEs to develop an environmental management system in their production processes, (ii) Assisting SMEs to apply concepts of EMSs in their actual operations in order to reduce pollution and comply with regulations while saving costs and increasing productivity, (iii) Developing environmental awareness among SMEs entrepreneurs, (iv) Laying a solid foundation upon which SMEs could base a further step towards international standards such as ISO 14001 or EMAS[2].An EMS helps an

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organization address its regulatory demands and non-regulated issues, such as energy conservation, and can promote stronger operational control and employee stewardship [3].

1.1 Environmental management system history

The environment has been a topic of debate dating hundreds of years. In the 1300's UK Parliament passed laws to control the smell from Thames River polluting their own air. However, the environmental concerns were increased due to the Industrial Revolution of the 18th and 19th centuries. Public outcries over smoke pouring from the stacks of coal burning factories, along with the eventual expansion of the petroleum industry, led to a growing concern and requirement for the implementation of corrective actions. During 1970's due to several external factors like the increased of regulatory pressure for environmental protection, the negative publicity on industries, the concerns from the citizens over the environmental impacts from the industrial processes, forced a number of industries to adopt on a voluntary base, environmental auditing programs which after were the base for the adoption of EMS[4]. In 1987, the United Nations World Commission on Environment and Development published a report called "Our Common Future", which first used the term "sustainable development" and called on industry to develop effective environmental management systems. A few years later in response to public support from more than 50 world leaders, the United Nations Conference on Environment and Development (UNCED) was arranged in Rio de Janeiro in 1992. This was known as the "Earth Summit" where a call for improved environmental management was established [5].In 1993 the European Commission produced a regulation on environmental management and auditing with the Eco-Management and Audit Regulation (1836/93/EC). This include the Eco-Management and Audit Scheme (EMAS) [6].At the same time the International Organization for Standardization (ISO) created a new technical committee known as TC 207 to develop an international EMS standard, having in mind other standards, environmental management tools and several audit techniques. In 1996, the ISO 14001 EMS specification was adopted and published [7,8]. Through the years, except the above standards, a number of related EMSs were also developed and established around the world (Table 1).

Table1: EnvironmentalManagement Systems

Acronyms		Description
ISO 14001	International Standard organization	EMS
BS8555	British Standard	Guide to the phased implementation of an EMS including the use of environmental performance evaluation
EMAS	Eco-Management and Audit Scheme	A voluntary environmental management instrument, which was developed in 1993 by the European Commission
Green Key		A voluntary eco-label award for hotels
LCA/ ISO 14040	Life cycle assessment	Product standard (covers life cycle assessment (LCA) studies and life cycle inventory (LCI) studies)
ISO 14020	Environmental labels and declarations	Establishes guiding principles for the development and use of environmental labels and declarations
Eco label		Identify products and services that have a reduced environmental impact throughout their life cycle, from the extraction of raw material through to production, use and disposal

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1.2. Environmental management system ISO 14000

ISO 14001 is a worldwide tool potentially applicable from all the organizations (governmental and non-governmental) in order to improve the management of their environmental aspects and reach a continuous improvement of environmental performance [9].The implementation of this type of standards is in a voluntary based, although in some economy sectors received pressures from its clients [10]. According to the annual survey, organized by ISO on December 2014, 324148 facilities worldwide had received ISO 14001 certification [11,12].

ISO 14001 is a process standard and accordingly it specifies the characteristics of the components of a management system. Thorough the standard the organization developed its environmental policy, set specific objectives and targets, as well as implement a program to achieve those objectives. Moreover the organization monitor and measure the program's effectiveness, correct problems, and conduct reviews aimed at improving the EMS[13].It follows the Deming's well known Quality Management approach of ''Plan, Do, Check and Act'' an iterative four-step management method used in business for the control and continuous improvement of processes and products (Figure 1).

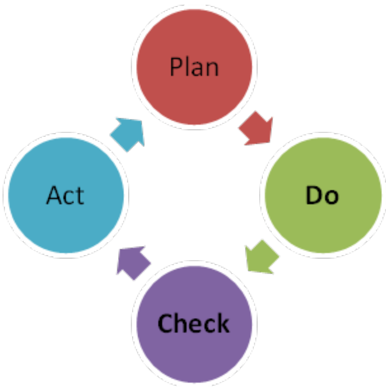


Figure 1:PCDAcycle[14]

The purpose of this paper is to analyse the barriers that arise during the implementation of an integrated and efficientEMS in a bakery-confectionary industry in Cyprus, in the framework of ISO 14001.

2. METHODOLOGY

For the evaluation of the implementation of the requirements of the ISO 14001 standard, the results that independent certification body were provided to the management team of the organization were taken into consideration (Table 2) for a period of 8 years (2008-2015).

The certification of a system is the recognition that the system meets a specific requirement of the proposed standard. The certification is granted by a certifying agency accredited by a supervisory body[15].The external audit takes place by the independent certification bodies are based in the requirement of the ISO 19001 which set the guidelines for the management systems auditing. Each certification has duration of three years and the external audit takes place at least once a year in order to find out if a continual improvement is exist and if the requirements of the specific standard still in place.The audit process enables continuous improvement in an EMS because it identifies non-conformities, highlights opportunities for improvement, and documents how the EMS encourages positive practices[16].Non-conformity are divided into three categories: a) observations, which are suggestions for improvement given by the inspector, b) minor non-conformity, which the organization needs to take corrective actions until the next evaluation and c) the major non-conformity, which the organization have to take actions in a period no more than 3

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months, otherwise if the non-conformity can't be closed then no certification is given to the organization.

Table 2: Basic paragraphs of ISO 14001:2004 [17]

	ISO 14001:2004		ISO 14001:2004
0	Introduction	4.4.2	Competence, training and awareness
1	Scope	4.4.3	Communication
2	Normativereferences	4.4.4	Documentation
3	Terms and definitions	4.4.5	Control of documents
4	Environmentalmanagementsystemrequirements	4.4.6	Operational control
4.1	General requirements	4.4.7	Emergency preparedness and response
4.2	Environmentalpolicy	4.5	Checking
4.3	Planning	4.5.1	Monitoring and measurement
4.3.1	Environmentalaspects	4.5.2	Evaluation of compliance
4.3.2	Legal and otherrequirements	4.5.3	Non conformity, corrective action and preventing action
4.3.3	Objectivestargets and programmers	4.5.4	Control of records
4.4	Implementation and operation	4.5.5	Internal audit
4.4.1	Resources, roles, responsibility and authority	4.6	Management review

3. RESULTS AND DISCUSSION

The data were analyzed from the reports given to organizations on a yearly basis by the independent certification bodies. Those reports, present in detail the progress of the organization compared to the implementation of the requirements of the EMS. Also record the non-conformities arising during the audit which is based on the paragraphs (and their subsections) of the standard (Table 2).

Figure 1 present the numbers of observations in relation with the paragraphs of ISO 14001:2004 for the period of 8 years. Most of the audits indicated that the observations were related to the paragraphs 4.4.2 focus on the competence, training and awareness (for the years 2009,2013,2014), 4.4.6 focus on the operational control (for the years 2008,2009,2012,2015), 4.5.3 focus on non-conformity, corrective action and preventing action (for the years 2010,2011,2014) and 4.5.4 which focus on control of records (for the years 2009,2013,2014). As on 2009 were the first year of the ISO 14001 implementation 7 observations were identified focuses on the above paragraphs, while on 2011 (after from 3 years implementation) were identified 4 of those and 5 on 2014.

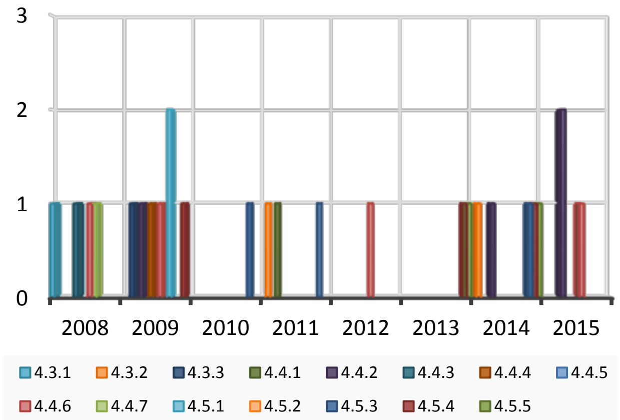


Figure 1: Number of Observations according the requirements of ISO 14001:2004

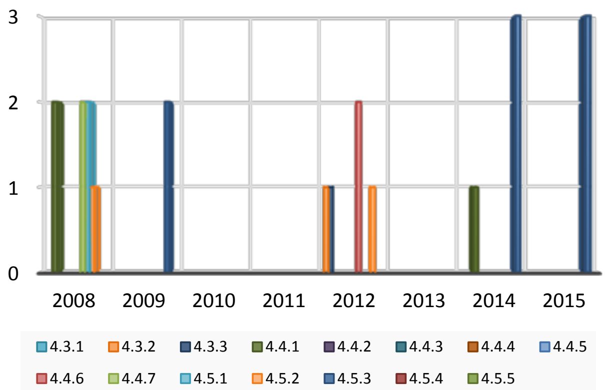


Figure 2: Number of Minor Non-conformities according the paragraphs of ISO 14001:2004

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Even though minor non conformities (Figure 2) were observed during the yearly survey audit (2008 were identified large numbers on minor non-conformities) those were less than the observations. Those minor non-conformities, needs further attention in order to avoid any inconsistencies from the ISO 1401 requirements. Those inconsistencies in case that no further attention will be given will turn on major conformities. Figure 2 indicated that the requirements of 4.5.3 paragraph were the most relevant and frequently issue.

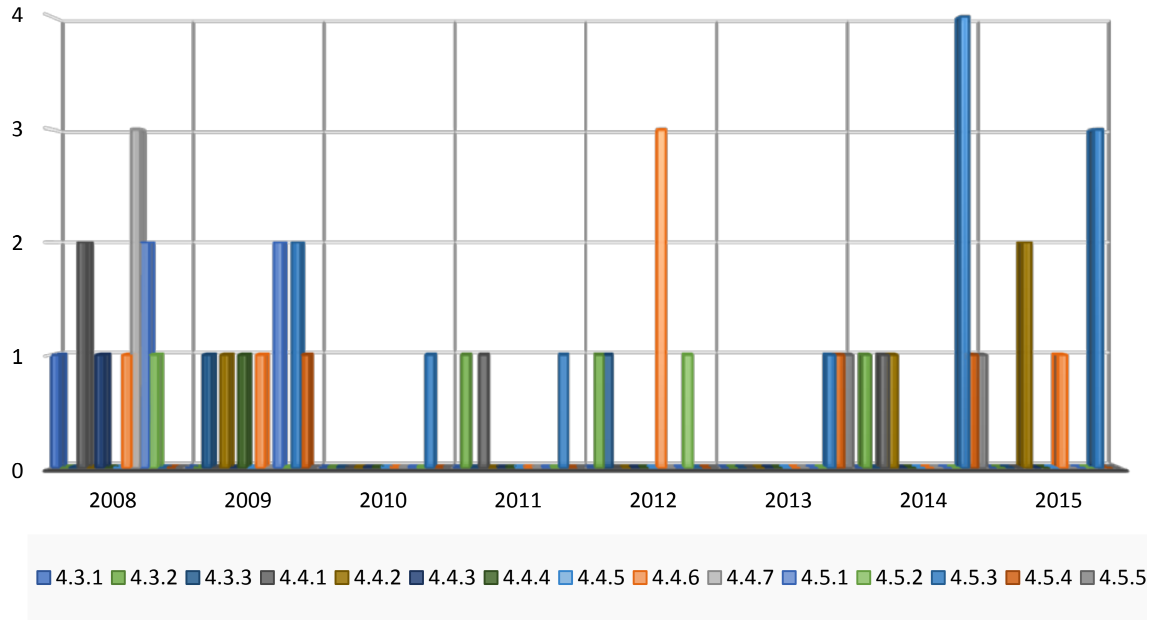


Figure 3: Total number of observations, minor and major non conformities

As indicated in Figure 3 no differences were observed on the total numbers of observations and non-conformities (minor and major) comparative with the years 2008, 2009, 2011, 2014. Totally and for the 8 years in reverse series (Figure 3) the requirements of the paragraph 4.5.3 received 12 numbers of observations, minor and major non conformities, followed by 4.4.6 with 6 while the rest paragraphs presented with 2-4 number of observations, minor and major non conformities.

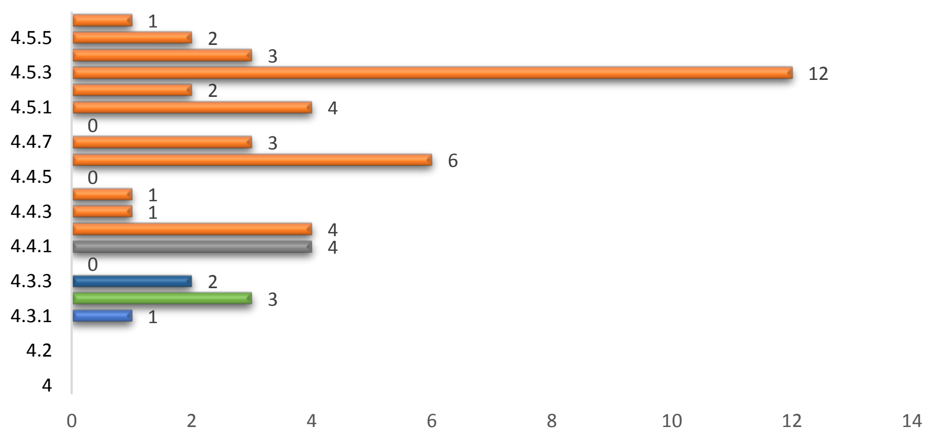


Figure 3: Total number of observations, minor and major non conformities overall for the eight years

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The analysis of the data indicates that the implementation of the requirements of a standard presents number of difficulties and obstacles. It is obvious that the main problems concern: a) 4.5.3 non conformity, corrective action and preventing action (i.e.no corrective actions about the previous inspection observation/non conformities), b) 4.4.6 operational control (i.e.growing plants next to the oil and gas storage area, oil containers were found out of the planned disposal) c) 4.5.1 monitoring measurement (i.e. non-compliance with certain legislations), d) 4.4.1 resources, roles, responsibility and authority (i.e. roles and responsibilities were not defined)and e) 4.4.2 competence, training and awareness (i.e. there is not documentation about training).

The main issue for the implementation of the requirements of ISO 14001 is consider to be paragraph 4.5.3 according to Searcy et al (YEAR) which indicated that the most common weaknesses has to do with the top manager vision which doesn't demonstrate how important is. Moreover according to the same researcher is that the problem(s) is/are been solved without any in depth investigation why the problem(s) was/were appears. Probably an explanation for this issueis the fact that the standard does notprovide and even more prescriptive clear distinction between a major and minor non conformity which remain to the Auditor to justify it is consider to be minor on major non confirmative indicated how subjectively is the opinion of the auditor.

Total cost according to [18] is consider to be one of the main issue that the management team take into consideration when a decision must take to apply or not the standard and furthermore if the system is being applied the same issues is presented when minor or major non conformity is being identified during the audit process and corrective action must be taken. Hence, lack of vision and specific goals (qualitative and quantitative) of the leadership and/or the management team of the organization, resulting to improper and ineffective implementation of the system (reference). Government support(i.e special tax exemption for ISO 14001 certification and consultation fee)and stakeholder demand as well as the fact that ISO 14001 is not a legal requirement constitute the most relevant factors hindering the adoption of the standard [19] from several economical activities.

In order to control and monitor the above non-conformities, each organization should change the way faced the system requirements. Specifically, leadership must develop a long-term strategic planning which through this each organization will seek to define roles and responsibilities to each employee regarding their obligations in implementing the system, to establish continuing education programs in the framework of lifelong learning and moreover to choose suppliers who will satisfy specific environmental requirements (such as the implementation of an environmental management system in order to minimize their environmental impact by taking actions such as waste prevention, recycling etc)

According to Zorpas (2010), motivations are needed in any organizations to implement EMS as well as to identify their environmental responsibilities. Those motivations has to do with the reduction of taxes (the most catchable one), as well as with personal (but not ethical) vies and believes.

4. CONCLUSION

Any EMS specifies requirements which an organization has to implement to reduce its environmental impact. An EMS can be a powerful tool for organizations to improve its environmental performance and increase its business efficiency. The implementation of an EMS it's not simple and easy. Economical and the typical structural of the organizations are the most significant incentives to motivate the employees and the management to adopt EMS. Additionally the fact that the implementation of a standard is not a legal requirement and there is no any requirement or demand from customers or stakeholders constitutes effect negative result on applying the standard. It is therefore essential to identify effective and realistic incentives as mentioned above, to encourage SMEs primarily to implement EMS. SMEs seem to need support

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and guidance, in particular for the environmental review and environmental aspects and significance evaluation. Moreover the collaboration between the leadership and employees it's crucial. Both of them must have a common purpose and goal to identify targets and objectives to minimize their environment impact and operated their procedures in a sustainable way.

References

[1] Liberty J., Echiegu E., 2015. An Appraisal of the Environmental Impacts of Food Processing Industrial Waste in Nigeria .*Journal of Natural Sciences Research* www.iiste.org ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online) Vol.5

[2] Zorpas A., 2010. Environmental management systems as sustainable tools in the way of life for the SMEs and VSMEs. *Bioresour. Technol*, **101(6)** 1544-1557

[3] Yin, H., Schmeidler, P., 2009. Why do standardized ISO 14001 environmental management systems lead to heterogeneous environmental outcomes. *Business Strategy and the Environment* **18**, 469-486

[4] Ellis J., 2014. A History of ISO 14001 2014 (http://www.greenelement.co.uk/) (accessed 16/3/2016)

[5] Voukkali I., Loizia P., 2015. Policies and Legislation. In: Sustainability Behind Sustainability , Eds A.A.Zorpas. Nova Science Publishers Inc, pp 7-16

[6] EMAS, 2011. European Commission. Brussels, Belgium. http://ec.europa.eu/environment/emas/index_en.htm.

[7] International Standard organizations (http://www.iso.org/iso/home.html)(accessed 17/3/2016)

[8] Marimon F., Llach J., Bernando M., 2011. Comparative analysis of diffusion of the ISO 14001 standard by sector of activity. *Journal of Cleaner Production* **19** 1734-1744

[9] Testa F., Rizzi F., Daddi T., Gusmerotti M.N., Frey M., Iraldo F., 2014. EMAS and ISO 14001: the differences in effectively improving environmental performance. *Journal of Cleaner Production* **68**, 165-173

[10] Bernardo M., Simon A., Jose Tarv J., Molina-AzorvnF.J., 2015. Benefits of management systems integration: a literature review. *Journal of Cleaner Production***94**, 260-267

[11] Arimura T., DarnallN,GanguliR.,Katayama H., 2016. The effect of ISO 14001 on environmental performance: Resolvingequivocal findings. *Journal of Environmental Managemen*t **166** 556-566

[12] International Organisation for Standardisation, 2015. The ISO Survey of ManagementSystem Standard Certifications 2014. ISO, Geneva, Switzerland.

[13] Mezinskaa I., Strodeb S., 2015. Emerging horizons of environmental management in food sector companies. *Procedia - Social and Behavioral Sciences***213**, 527 – 532

[14] BulsulG.K (www.bulsuk.com) (accessed 15/3/2016).

[15] Jose de Oliveira O.,(2013).Guidelines for the integration of certifiable management systems inindustrial companies. *Journal of Cleaner Production***57** 124-133

[16] Searcy C., Morali O., Karapetrovic S., Wichuk K., McCartney D., McLeod S., 2012 Challenges in implementing a functional ISO 14001 environmental management system. *International Journal of Quality & Reliability Management***29 (7)** 779-796

[17] Cassells S., LewisV.K.,Findlater A., 2012. An exploration of ISO 14001 uptake by New Zealand firms.*International Journal of Law and Mana*gement **54 (5)** 345-363.

[18] International Organisation for Standardisation (2004). Environmental management systems – Requirements with guidance for use (ISO 14001),

[19] Massoud A.M., Fayad R., El-Fadel M., Kamleh R., 2010. Drivers, barriers and incentives to implementing environmental management systems in the food industry: A case of Lebanon. *Journal of Cleaner Production***18**, 200–209

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Naturally occurring asbestos in the southern Apennines: quick μ-Raman Spectroscopy identification as a tool of environmental control

M. C. Dichicco*, A. De Bonis, G. Mongelli, G. Rizzo, R. Sinisi

Department of Sciences, University of Basilicata, 85100 Potenza, Italy
*Corresponding author: Email: maria.dichicco@unibas.it

Abstract

For many years, great attention has been paid to the relationships between some respiratory and digestive system diseases and the asbestos-like minerals within different environmental matrices. These harmful minerals generally occur as naturally exposed friable fibres that can be easily released into the environment as a consequence of both natural processes and anthropogenic activities. The aim of this paper is to evaluate the best analytical tool for an easy, quick and safe analysis of the asbestos-bearing rocks. Therefore, we compared methods and results derived from the X-ray powder diffraction analysis and the *μ*-Raman spectroscopy performed on the asbestos-rich serpentinite rocks of the Pollino Massif (southern Italy). The more detailed mineral identification, lower acquisition times, and higher safety levels of the spectroscopic technique have been documented suggesting the latter method is preferable to the most common X-ray powder diffraction for the study of health dangerous materials.

Keywords: serpentinites; asbestos minerals; toxicity; Pollino massif; μ-Raman spectroscopy.

1. INTRODUCTION

Fibrous silicate minerals belonging to the serpentine and amphibole mineral groups are flexible, heat-resistant, and chemically inert. When their habitus [long (> 5 µm) and thin] and dimensions (diameter < 1µm) are inhalation-compatible can cause high mortality neoplasms (asbestosis, lung cancer, and malignant mesothelioma) [1, 2, 3, 4].

Among these, malignant pleural mesothelioma (MPM) is an uncommon neoplasm typically originating by chrysotile, crocidolite, amosite, or tremolite that are considered to be the most dangerous carcinogen fibres. Most of the asbestos-induced mesotheliomas occurs in the industrial environment being linked mainly to a protracted asbestos exposure of workers engaged in extracting and manufacturing of asbestos-containing materials [5]. However, it is currently recognized that asbestos-caused health problems may also develop in non-occupational circumstances [5, 6, 7]. The regular environmental exposure in the neighbourhood of industrial sources (asbestos mines and mills, asbestos processing plants), the passive exposure in buildings containing asbestos, and the natural environmental exposure to geological sources are some examples [8]. The environmental exposure is of special and broad interest because can starts during childhood and be lifelong. There are several studies which demonstrate the strong linkage between mesothelioma and environmental asbestos exposure especially in people living in close vicinity of naturally occurring asbestos sources and/or having direct contact with asbestos [9, 10, 11, 12].

In some areas of southern Apennines (Basilicata region, southern Italy) where several cases of mesothelioma were documented [13], the Regional Operating Centres of Basilicata (COR) the Italian National Mesothelioma Register (ReNaM), and the COR Puglia conducted a complete

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epidemiological study. In detail, 17/90 mesothelioma cases refer to people living in areas close to natural outcrops of asbestos-bearing rocks [14]. Asbestos-bearing rocks, chiefly serpentinites, can release significant amounts of fibres into the air, water, and soil during the quarry operations, most commonly as a result of extraction procedures including the stacking, storing, and grinding of excavated materials. In this regard, the presented study focuses on several natural, serpentinite outcrops within quarries developed in the low-grade metamorphic ophiolites of the Pollino massif (Calabria-Lucania boundary, southern Italy). These rocks were used as pilot samples for the identification of asbestiform minerals (serpentine as well as amphibole mineral phases) by mean of μ-Raman spectroscopy and X-ray powder diffraction (XRPD) analysis to compare the analytical procedures as much as their results, with the final aim to assess the better method for the study and the identification of health dangerous materials.

2. THE ASBESTOS-BEARING ROCKS OCCURRENCE

This study focused on serpentinites rocks that represent the lherzolitic to harzburgitic, upper mantle basement of the Internal Liguride sequence consisting of Neotethyan Ocean fragments uplifted during formation of the Appenine belt [15, 16, 17, 18]. Serpentinites are englobed in a methamorphosed ophiolitic suite where mafic dykes and medium to high-grade metamorphic rocks such as amphibolite, gneiss, granofels as well as gabbro and pillow lava basalts occur [19]. The ophiolite suites suffered two major phases of ocean floor polyphase metamorphism [19] during which ductile deformation, recrystallization, and hydrothermal metasomatism processes favouring the formation of the fibrous minerals as main mineral phases of bulk rocks and vein infill.

In southern Apennine, at the Calabria-Lucanian boundary (Figure 1a), the asbestos-bearing serpentinites are widely exposed at several active and abandoned quarries (Pietrapica quarry, Timpa Castello quarry, Fagosa quarry, Fosso Arcangelo, San Severino Lucano, Rovine Convento Sagittale localities, Monte Nandiniello and Ghiaia quarry) (Figure 1b).

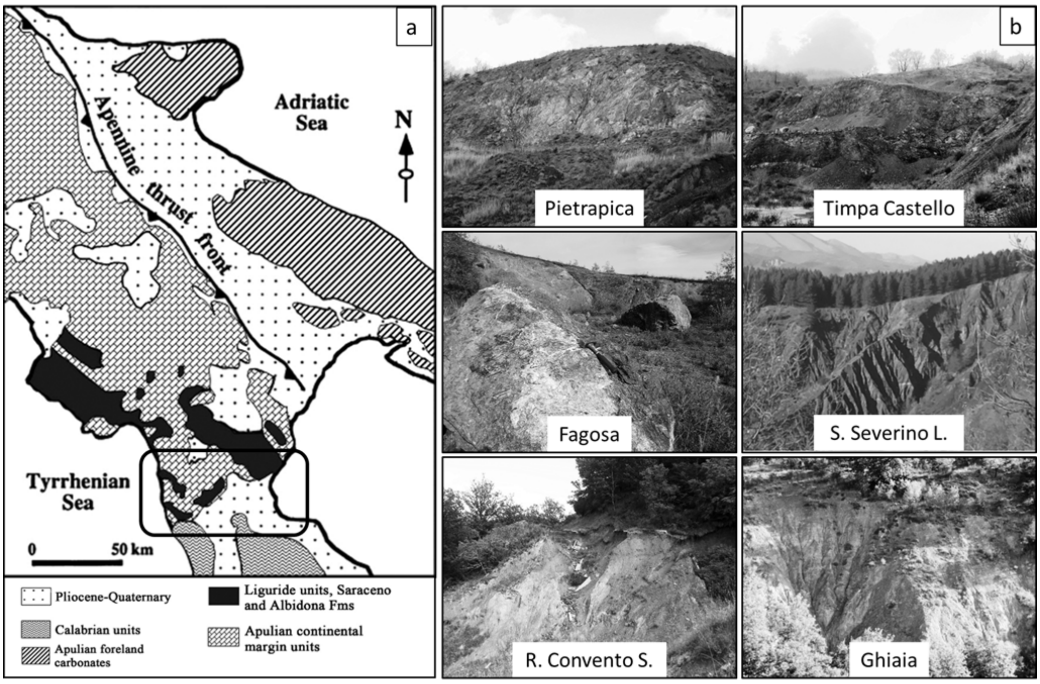


Figure 1. (a) Geological sketch map of the southern Apennines (modified after Sansone et al., [[19]]) and location of the study area. (b) Representative quarries at the Calabria-Lucanian boundary.

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As recently documented by Dichicco et al. [20], based on their macroscopic features, the serpentinite rocks can be classified as cataclastic and massive. Cataclastic serpentinites are ubiquitous throughout all the examined sites and include the massive ones. Cataclasites exhibit high degree of fracturing and deformation that form cohesive serpentinites and/or fault breccias. Several generations of cross-cutting fractures were observed as well. The fractures are almost completely filled by exposed white and grey fibrous minerals. The fibres are soft and friable and easily released by water runoff and weathering processes. Two fibre types have been identified in the outcrops: 1) big and elongate fibres developed over slickensided surfaces (Figure 2a); 2) very fine-grained fibres forming a network pervading the whole rock (Figure 2b). Conversely, the massive serpentinites show a low fracturing and deformation degree and any exposed fibrous minerals. However, the cataclastic and massive serpentinites have homogeneous mineral compositions. They are mainly composed by, in order of decreasing abundance, serpentine, tremolite-actinolite, chlorite, magnetite and other Cr-spinels, with minor but ubiquitous calcite, dolomite, and clay minerals.

At microscale, serpentinites are characterised by serpentine + magnetite mesh-texture with a core of relict olivine grains. Along cleavage planes, lamellae and fibres of serpentine are spread on bastite pseudomorphs after orthopyroxene. The amphibole minerals, being of the tremolite-actinolite series [20], show acicular and elongated habitus. These minerals are present in veins as much as in the matrix of analysed rocks forming crowns around clinopyroxene porphyroclasts. The serpentinites are crosscutted by a micro-network of nanometre to millimetre veins filled by fibrous serpentine and serpentine ± amphiboles, amphibole minerals, calcite ± amphiboles, chlorite, and prehnite.

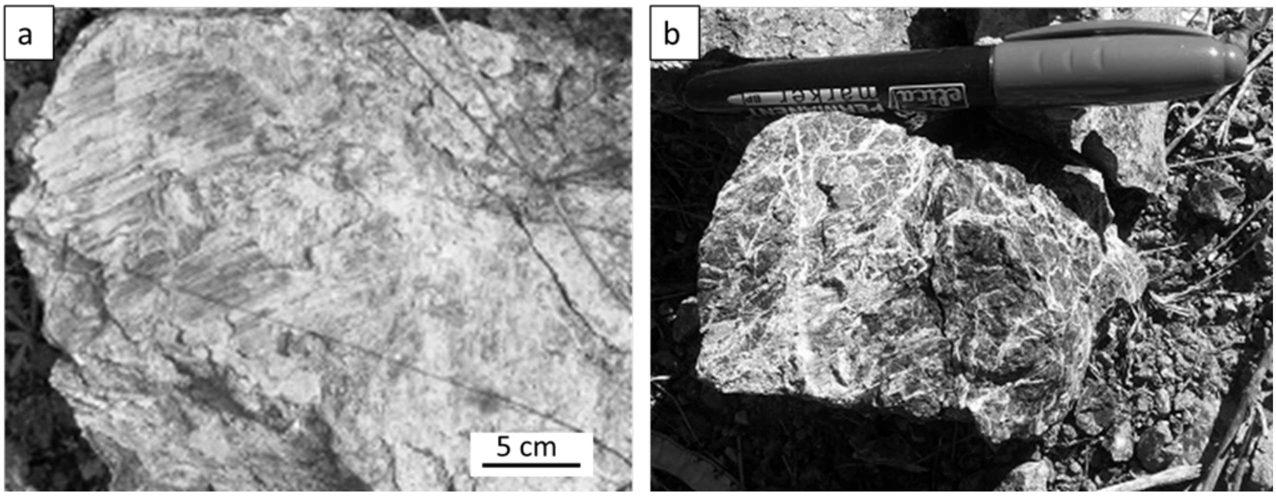


Figure 2. (a) Centimetre fibres developed over slickenside surfaces (Fagosa quarry). (b) Very fine-grained fibres along a fracture network pervading the full rock (San Severino Lucano quarry).

3. ANALYTICAL METHODS

Thirteen samples of serpentinite rocks from the Frido Unit were collected at Fosso Arcangelo and Rovine Convento Sagittale sites (Figure 1). Based on field observations, studied serpentinites were concerned by both cataclastic structure and veins with different thickness pervading the whole rocks.

The XRPD analyses were performed at the Department of Sciences, University of Basilicata, on randomly oriented powdered samples of both bulk rocks and vein infill, using a Siemens D5000 diffractometer with CuKα radiation, 40 kV and 32 mA. Data were recorded between 5^o and 70^o 2θ for the bulk rock samples and from 15 to 70°2θ for the vein infill, with stepsize of 0.02° and speed of two seconds per step in order to optimize the signal/noise ratio. The mineral phases identification was realized by mean of X'Pert HighScorePlus software using the PDF-2 (2005) database. Raman

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spectroscopy measurements were performed at the Department of Sciences, University of Basilicata, using a Horiba Jobin-Yvon LabRam HR800 spectrometer equipped with a HeNe laser source with a wavelength of 633 nm, a CCD detector operating at -70^{o}C and an edge filter that exclude from detection shift below 150 cm^{-1}. A spectral resolution of 4 cm^{-1} was obtained by a holographic grating with 600 lines/mm. Correct calibration of the instrument was verified checking the position of the Si band at ± 520.7 cm^{-1}. Output laser power was 20 mV, and measurements were performed using optical microscope Olympus with objective of 10X, 50X and 100X. Analyses were carried out on macroscopic samples. Spectra result from the average of 5 acquisitions of 10 s to optimize the signal/noise ratio. Two regions of the Raman spectra were investigated: 150-1.200 cm^{-1} for structural bonding characterization and 3.500-3.800 cm^{-1} for the characterization of the hydroxyl groups.

4. RESULTS AND DISCUSSION

4.1 XRPD assessment

The X-ray diffraction analysis of powdered bulk rock allowed clearly the recognition of the serpentine and amphibole-like minerals (actinolite, d = 8.31 Å; tremolite, d = 2.94 Å) that are the dominant phases, followed by 2 : 1 phillosilicate (clinochlore, d = 4,74), with minor amount of iron oxides (magnetite, d = 2.52). Different carbonate phases were also identified as calcite (d = 3.04), aragonite (d = 3.38), and dolomite (d = 2.88) (Figure 3). In addition, the diffraction patterns of veins show that amphiboles (actinolite; tremolite), and carbonate minerals are the main components. Calcite and aragonite with minor amount of dolomite and rhodochrosite (d = 2.80) are also identified in these samples (Figure 3). The XRPD analysis does not allow accurately the identification of different serpentine polytypes, because the position of the main diffraction peaks, in turn related to the chemical composition of the each polytype, is very similar.

4.2 µ-Raman spectroscopy

µ-Raman measurements were performed to further identify minerals that compose the serpentinite. This technique is particularly efficient for a quick and reliable identification of serpentine minerals (lizardite, antigorite, chrysotile and polygonal serpentine), as well as amphibole polymorphs (tremolite – ferro-actinolite) [21, 22]. Results show that lizardite and chrysotile, are the dominants serpentine variety. In both fibrous antigorite and chrysotile the main peaks in the Raman spectrum are related to the symmetric Si-O_b-Si stretching and SiO_4 bending modes, which occur at 687 and 378 cm^{-1} in antigorite, and 694 and 388 cm^{-1} in chrysotile, respectively [[21], [22]]. Two strong peaks at 230 cm^{-1} in antigorite and 235 cm^{-1} in chrysotile are related to the O-H-O vibrational modes. Furthermore, antigorite may also be easily distinguished from chrysotile on the basis of the 1.045 cm^{-1} antisymmetric Si-O_b-Si stretching mode (Figure 4a). In the spectral region associated to vibrational modes of the OH groups, antigorite and chrysotile are characterized by very different □-Raman spectra. Antigorite shows two main bands at 3.672 and 3.701 cm^{-1}, whereas chrysotile shows a major, asymmetric band at about 3699 cm^{-1}, with a tail toward lower frequencies, and a less pronounced peak at about 3.691 cm^{-1} [23] (Figure 4b). In addition, light green serpentine was identified as polygonal serpentine. It shows quite similar Raman spectrum to those of the lizardite at low wavenumbers, but strongly differs at high wavenumbers (3.500 to 3.800 cm^{-1}). At high wavenumbers the polygonal serpentine is characterized by a large peak composed by two bands centered at 3.693and 3.704 cm^{-1} [[24], [23]] while lizardite presents a sharp peak at 3.685cm^{-1} and a lower one at 3,708cm^{-1} (Figure 4b, Table 1). The low wavenumber spectra of different serpentine species are very similar and the attribution can be complex since variation of the chemical composition can induce variation in peaks position and relative intensities. On the other hand the analysis of the vibration of the OH groups allows to easy discriminate among different polymorph species [25].

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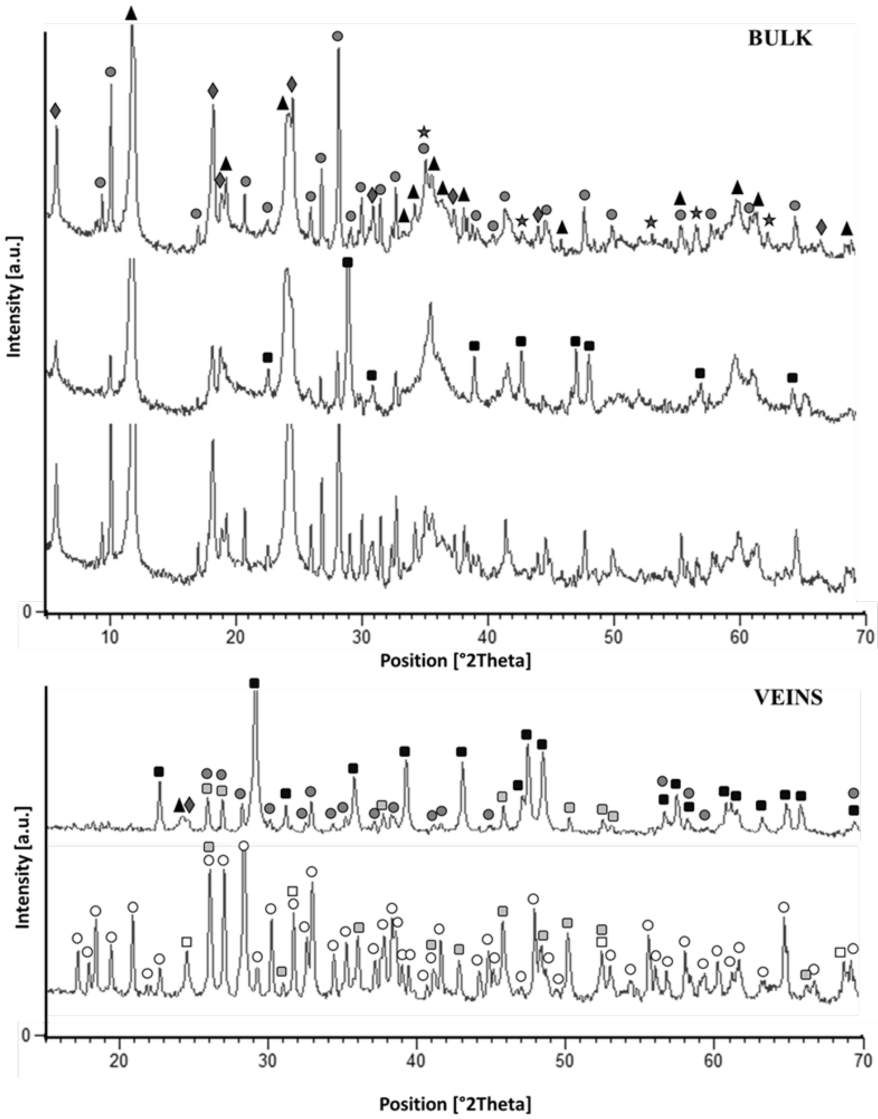


Figure 3. XRPD patterns of selected bulk and vein serpentinite samples. Legend: filled triangle = serpentine; filled circle = tremolite; empty circle = actinolite; filled rhombus = clinochlore; black square = calcite; gray square = aragonite; empty square = rhodochrosite; star = magnetite.

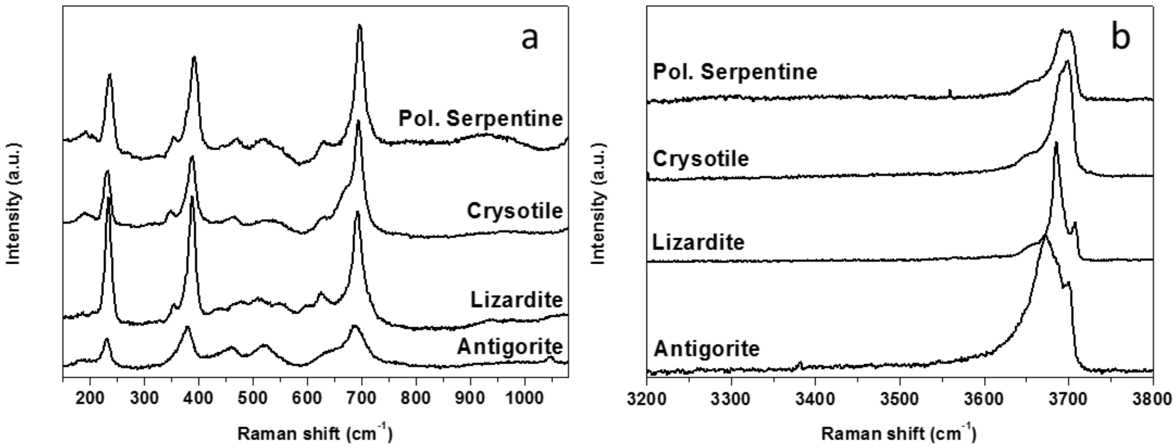


Figure 4. Raman Spectra at low (a) and high (b) wavenumbers of serpentine minerals.

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The main feature of the Raman spectra of tremolite – ferro-actinolite minerals in the low-wavenumber region (100-1.200 cm^{-1}) is the A_g symmetry mode at nearly 675 cm^{-1}, related to Si-O symmetrical stretching. This mode, when substituting Mg^{2+} with the heavier Fe^{2+}, downshifts from 675 cm^{-1} in pure tremolite to 667 cm^{-1} in Fe-rich actinolite (ferro-actinolite) [[26]]. In the high-wavenumbers region (3.500-3.800 cm^{-1}) a number of OH stretching bands (from 1 to 4) may be present. The number and relative intensity of these bands depend on the X value ($X = Mg/(Mg+Fe^{2+})$). According to Chen et al. [27] and Bersani et al. [26], for $0.9 \leq X \leq 1$ we have tremolite, for $0.5<X<0.9$ actinolite, and for $X<0.5$ ferro-actinolite (rare). In nephrites the OH group vibrations are influenced by the population of the 3 metal sites where Fe^{2+} or Mg^{2+} could be present [27]. When only Mg is present (as in pure tremolite), only one peak (at 3.675 cm^{-1}) is observed. As the amount of iron increases, the other peaks, related to different combinations of Fe^{2+} and Mg^{2+} in the sites close to OH, arise at lower wave numbers [[26]].

In our spectra symmetric and antisymmetric Si-O-Si stretching modes of fibrous amphibole give peaks at about 675 cm^{-1} and 1.062 cm^{-1}, which are also the strongest ones. O-H-O vibrations produce one other strong peaks at about 223 cm^{-1}. In the OH vibrational region, amphibole shows two peaks, the most intense at 3.675 cm^{-1}, and the second at 3.660 cm^{-1} (Figure 5, Table 1).

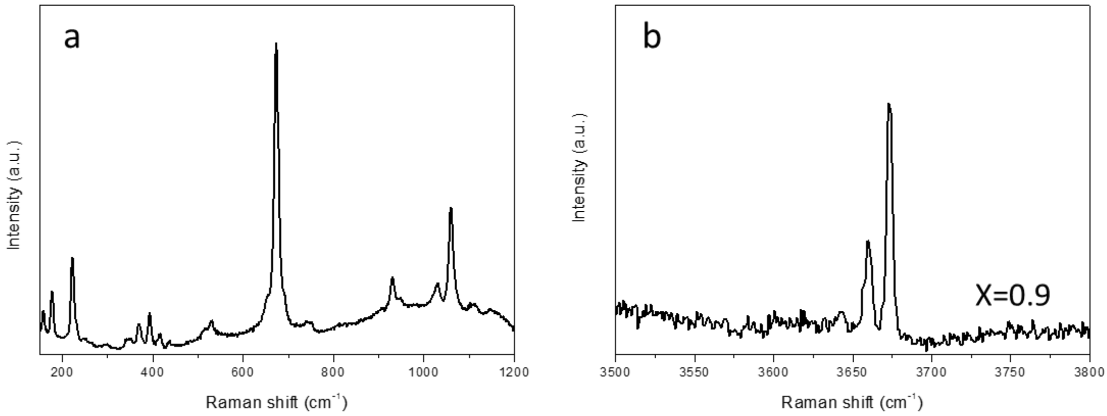


Figure 5. Raman Spectra at low (a) and at high (b) wavenumbers of the tremolite.

Therefore, the number and relative intensity of these bands represent almost pure tremolite with a small percentage of Fe^{2+}. In fact, as reported by Bersani et al. [26], X value can be estimate from Raman spectra considering: $X=(A_{12})/(1/3+A_{12})$, where A_{12} is the ratio between the areas of OH Raman bands at about 3.675 and 3.660 cm^{-1}. In Figure 5 is reported the composition (X value) estimated from the areas of the OH bands.

Table 1. Diagnostic peaks in μ-Raman spectra of serpentine and amphibole minerals

Minerals								
Pol. Serpentine	236	350		696	1121	3646	3693	
		394					3704	
Chrysotile	235	345		694	1106	3649	3699	
$Mg_3Si_2O_5(OH)_4$		388					3691	
Lizardite	233	350	514	628	1091	3654	3685	
$Mg_3(OH)_4Si_2O_5$		389		698				3708
Antigorite	230	378	520	687	1045			3672
$(Mg,Fe^{2+})_3(OH)_4Si_2O_5$								3701
Tremolite	175	367	529	675	930	3660	3675	
$Ca_2Mg_5Si_8O_{22}(OH)_2$	223	392			1030			
		415			1062			

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5. CONCLUSIONS

In this study the cataclastic and massive asbestos-bearing serpentinites from southern Apennines were investigated. These rocks widely occur at natural outcrops as well as in active and abandoned quarries where a harmful exposition of soft and friable fibrous minerals (easily released into the air, water, and soil) was documented. In this realm, it is very important to find an analytical tool of environmental control useful for the identification of the asbestos minerals. Therefore, two different techniques for mineralogical analysis, the XRPD and the μ-Raman spectroscopy, have been performed and compared. The results suggest both the analytical methods provide reliable data about the mineralogical composition of the serpentinite rocks. However, only the μ-Raman spectroscopy allowed the identification of the different serpentine polytypes and nephritic amphiboles. Besides, the μ-Raman method shows further advantages than the XRPD one. The μ-Raman spectroscopy, for instance, is a very quick technique because it requires acquisition times (only few seconds) much lower than those needed for the XRPD (some hours). Finally, we believe that, to study rocks containing minerals hazardous for the human health, the μ-Raman spectroscopy is easier and safer than the XRPD, because the spectroscopic analysis can be performed directly on the macroscopic samples avoiding all harmful rock treatment activities, such as crushing and pulverizing, which conversely are mandatory for the diffraction analysis.

References

[1] Brody, A.R., 2010. Asbestos and lung disease. *Am. J. Respir. Cell Mol. Biol.*, **42**, 131– 132.

[2] Jamrozik, E., de Klerk, N., Musk, A.W., 2011. Asbestos-related disease. *Intern. Med. J.*, **41**, 372–380.

[3] Liu, G., Cheresh, P., Kamp, D.W., 2013. Molecular basis of asbestos-induced lung disease. *Annu. Rev. Pathol.*, **8**, 161–187.

[4] Stayner, L., Welch, L.S., Lemen, R., 2013. The worldwide pandemic of asbestos-related diseases. *Annu. Rev. Public Health*, **34**, 205–216.

[5] McDonald, J.C., McDonald, A.D., 1996. The epidemiology of mesothelioma in historical context. *Eur Respir J.*, **9**, 1932–1942.

[6] International Agency for Research on Cancer (IARC), 1987. Monographs on the evaluation of carcinogenic risks to humans. Lyon: IARC. Overall evaluation of carcinogenicity: an updating of IARC Monographs. Sup **l.7**, 1–42.

[7] Lemen, R.A., Dement, J.M., Wagoner, J.K., 1980. Epidemiology of asbestos-related diseases. *Environ Health Perspect*, **34**, 1–11.

[8] Gardner, M.J., Saracci, R., 1989. Effects on health of non-occupational exposure to airborne mineral fibres. In: Bignon, J., Peto, J., Saracci, R., editors. Non-occupational exposure to mineral fibres. Lyon: *IARC Sci.Publ*; pp. 375–397.

[9] Baris, Y.I., Sahin, A.A., Ozesmi, M., Kerse, I., Ozen, E., Kolacan, B., 1978. An outbreak of pleural mesothelioma and chronic fibrosing pleurisy in the village of Krain/Urgüp in Anatolia. *Thorax*, **33**, 181–192.

[10] Langer, A.M., Nolan, R.P., Constantopoulos, S.H., Moutsopoulos, H.M., 1987. Association of Metsovo lung and pleural mesothelioma with exposure to tremolite containing whitewash. *Lancet*, **i**, 965–967.

[11] McConnochie, K., Simonato, L., Mavrides, P., Christofides, P., Pooley, F.D., Wagner, J.C., 1987. Mesothelioma in Cyprus: The role of tremolite. *Thorax*, **42**, 342–347.

[12] Luo, S., Liu, X., Mu, S., Tsai, S.P., Wen, C.P., 2003. Asbestos related diseases from environmental exposure to crocidolite in Da-yao, China I. Review of exposure and epidemiological data. *Occup Environ Med.*, **60**, 35–41.

[13] Pasetto, R., Bruni, B., Bruno, C., D'Antona, C., De Nardo, P., Di Maria, G., Di Stefano, R., Fiorentini, C., Gianfagna, A., Marconi, A., Paoletti, L., Putzu, M.G., Soffritti, M., Comba, P., 2004. Problematiche sanitarie della fibre anfibolica di Biancavilla. Aspetti epidemiologici, clinici e sperimentali. *Notiziario dell'Istituto Superiore di Sanità.*, **17**, 8-12.

[14] Massaro, T., Fiore, S., Dragonieri, S., Grimaldi, M.C., Pistillo, S., Cauzzillo, G., Musti, M., 2011. Pleura malignant mesothelioma among resident population in areas with natural occurring asbestos on Calabria-lucania border. *GeoMed – 4th International Conference on Medical Geology.*

[15] Gueguen, E., Doglioni, C., Fernandez, M., 1998. On the post-25 Ma geodynamic evolution of the western Mediterranean. *Tectonophysics*, **298**, 259-269.

[16] Cello, G., Mazzoli, S., 1999. Apennine tectonics in southern Italy: A review. *Journal of Geodynamics*, **27**, 191-211.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[17] Doglioni, C., Gueguen, E., Harabaglia, P., Mongelli, F., 1999. On the origin of west-directed subduction zones and applications to the western Mediterranean. In: Durand, B., Jolivet, L., Horváth, F., Séranne, M., (Eds) The Mediterranean basins: Tertiary extension within the alpine orogen. *Special Publications Geological Society*, London, **156**, 541-561.
[18] Patacca, E., Scandone P., 2007. Geology of the southern Apennines. In: Mazzotti, A., Patacca, E., Scandone, P., (Eds) Results of the CROP Project, Sub-project CROP-04 southern Apennines (Italy). *Bollettino della Società Geologica Italiana*, Special Issue, 75-119.
[19] Sansone, M.T.C., Rizzo, G., 2012. Pumpellyite veins in the metadolerite of the Frido Unit (southern Apennines-Italy). *Periodico di Mineralogia*, **81**, 75-92.
[20] Dichicco, M.C., Laurita, S., Paternoster, M., Rizzo, G., Sinisi, R., Mongelli, G., 2015. Serpentinite Carbonation for CO_2 Sequestration in the Southern Apennines: Preliminary Study. *Energy Procedia*, **76**, 477-486.
[21] Rinaudo, C., Gastaldi, D., Belluso, E., 2003. Characterization of chrysotile, antigorite and lizardite by FT-Raman spectroscopy. *Can. Mineral.*, **41**, 883-890.
[22] Groppo, C., Rinaudo, C., Cairo, S., Gastaldi, D., Compagnoni, R., 2006. Raman Spectroscopy as a rapid method for the identification of serpentine minerals from serpentinized ultramafics. *Eur. J. Mineral.*, **18**, 319-329.
[23] Auzende, A.L., Daniel, I., Reynard, B., Lemaire, C., Guillot, F., 2004. High pressure behaviour of serpentine minerals: a Raman spectroscopy study. *Phys. Chem. Minerals*, **31**, 269-277.
[24] Lemaire, C., 2000. Application des spectroscopies vibrationnelles à la détection d'amiante dans les materiaux et à l'étude des serpentines, Unpublished PhD, *Université de Paris 7*, Paris, 157.
[25] Petriglieri, J.R., Salvioli-Mariani, E., Mantovani, L., Tribaudino, M., Lottici, P.P., Laponti-Magoni, C., Bersani, D., 2015. Micro-Raman Mapping of the polymorphs of serpentine. *Raman Spectroscopy*, **46**, 953-958.
[26] Bersani, D., Andò, S., Scrocco, L., Gentile, P., Salvioli-Mariani, E., Lottici, P.P., 2014. Study of composition of amphiboles in the tremolite – ferro-actinolite series by micro-Raman and SEM-EDXS. 11th International GeoRaman Conference. Louis, Missouri, USA.
[27] Chen, T.H., Calligaro, T., Pagès-Camagna, S., Menu, M., 2004. Investigation of Chinese archaic jade by PIXE and μRaman spectrometry. Appl. Phys. A, **79**, 177-180.

Rural road construction and operation: impacts on cultivated land

G. Kollaros*, A. Athanasopoulou, V. Kollarou

Department of Civil Engineering, Democritus University of Thrace, 67132, Xanthi, Greece.
*Corresponding author: Email: gkoll@civil.duth.gr

Abstract

Rural road construction and improvements have dynamic impacts on farm productivity and crop choices. It has been shown that the improved roads reduced market prices of local crops. This research work examines ways that transportation decisions affect land use patterns, and the resulting economic, social and environmental impacts. These include direct impacts on land used for transportation facilities, and indirect impacts caused by changes to land use development patterns. Specific methods for evaluating these impacts in transport planning are described. Mitigation measures against land degradation induced by rural road construction are also discussed. A system of sub-programs has been developed to analyze the full geometric characteristics of a road project and assess the impact caused by both the construction and operation of roads to agriculture or farming lands.

Keywords: farm access road; rural road; farming; environmental impacts; crops

1. INTRODUCTION

A transportation mode is the means of mobility used to carry goods and persons from one place to another. Rural roads promote economic development, but they also facilitate deforestation and have important impacts on arable land [1]. To explore this tradeoff, land uses are explored depending on different physical characteristics. Probabilities of alternative land uses as a function of land characteristics are also estimated. Controls are incorporated for the endogeneity of road placement. Geographic information system techniques are appropriate for the selection of sample points at various intervals (usually1 kilometer). It seems that constructing roads in areas with agriculturally poor soils and low population densities may not be a viable proposition, causing habitat fragmentation and providing low economic returns.

The development of an area receives increased pressures by new infrastructure, especially roads. This feature is beneficiary for the economic support of development projects, but it is not positively acting on the surrounding environment and land uses. Thus planning and management of acceptable sites coupled with control is necessary, so as to avoid damaging pressure on sensitive sites [2]. Rural road projects, being usually small in scale, could probably generate adverse environmental impacts, both direct and indirect. Direct environmental impacts have their origin to activities related to construction and rehabilitation activities. Indirect environmental impacts are usually connected to the operation of improved roads (e.g. a rural road could facilitate the exploitation of mineral in remote sites and contribute in economic development of the particular area. However, adverse impacts could be generated without adequate enforcement of environmental regulation [3].

General hazards and risks are applicable to major road projects. However, some impacts may arise specifically as a result of the project (e.g. degradation after the completion of construction) [4]. All the time, the rural road network is under uncertainty due to various reasons. The presence of this network and its traffic flows offer access possibilities and they contribute in the economic growth,

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while on the other hand they cause fragmentation. The real ecological impact of this fragmentation depends on a variety of variables, such as the characteristics of the road and of the fauna species [5].

2. IMPACTS OF RURAL ROADS ON THE ENVIRONMENT

The road infrastructure can have various types of direct effect on its environment. The intensity of impact depends on specific types and characteristics of the:

(1) road (width, kind of pavement, mitigating measures); based on their function, road networks could be distinguished in motorways, rural highways and minor rural roads [6, 7]. Minor rural roads are in their majority local collectors and access roads.
(2) traffic (speed, flow, composition by mode);
(3) verge (width, shape, surface, overgrowth); on a slope, wind velocity is increased and may also increase by some topography features leading to the requirement for protective measures [8]
(4) surrounding land uses (town, forest, agricultural land); and
(5) species (size, weight, food specialisation, home-range, dispersal ability, and rarity).

The physical existence of roads in the natural landscape creates new ecosystem limits, alters the hydrology dynamics and disrupts the natural processes and ecosystems. The maintenance of roads, as well as traffic, pollutes the surrounding space with various pollutants and noise. The main impacts of roads on ecology include [5]:

- Habitat loss.
- Disturbance, annoyance.
- Corridor creation; the greatest effects are located where a road crosses or is alongside wide corridors, while the least are where a small road is alongside the margin [9].
- Hindrance of locomotion (barrier effect).
- Mortality.
- Impacts on hydrology and aquatic habitats.
- Invasion of exotic species.
- Access facilitation in areas previously inaccessible.

3. PARTIAL MODEL OF RURAL ROAD IMPACTS IN CULTIVATED LANDS

The discrepancy between universal models and a proposed road alignment is resolved through the Environmental Impact Assessment achieved by various systems. A system of sub-programs of this type has been developed in the Transport Engineering Laboratory of the Democritus University of Thrace in order to analyze the full geometric characteristics of a road project and assess the impact caused by both the construction and operation of roads to agriculture or farming lands.

In the following paragraphs, the part of the software relating to the impacts on the environment due to the operation of roads whose alignment passes through cultivated sites or developed in agricultural manner areas will be analyzed. The goal is to highlight the dominant idea on which the software is based and the way the relationship between the user and the computer is interactively developed when data is imported as well as when the management of results is necessary.

The partial model explores the effect of roads during their construction and use on the agricultural production. The expected impacts are divided into two types of damage:

1. Total loss of agricultural surfaces.
2. Permanent degradation of agricultural products due to frost damage and food contamination

In the proposed model, the following input data are used (data in the form of thematic maps):

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- Rural land uses, i.e., thematic map with the frame outline of each variety and form of rural surface, as it is differentiated in terms of land use and sensibility of use in frost conditions and sensitivity in exhaust gases, a soil quality thematic map etc.
- Cold air sources, i.e., a thematic map with cold air frame outlines (soils with high evaporation, valleys with abundant waters, wide plains, fields, etc., where there is a temperature drop).

In addition, the following elements received by the road alignment program are required:

- Embankments
- Carriageway lane
- Cuts
- Embankments effect on cold air flow
- Contaminated areas.

If the road passes through agricultural surfaces, surface losses there exist; this will nullify any agricultural exploitation. The total loss of agricultural surfaces is calculated in two steps: (a) direct loss of agricultural land surfaces due to their occupation by the road and (b) the negative influence of the area segmentation.

Agricultural land surfaces are often directly lost due to their occupation by the road. As it can be seen in Figure 1, the total surface area, V, required by the road infrastructure is the union of surfaces:

$$V = A \cup B \cup C$$

where:

A is the surface area required for the construction of embankments, B is the surface of the carriageway lane, and C is the surface required for the construction of road cuts.

This result is finally introduced in the program (indication A in the flow diagram) and its intersection with the surface "agricultural land uses" (indication B in the flow chart) yields: (a) The direct loss of agricultural surface area from the road: intersection $A \cap B$ and (b) The remaining surfaces with agricultural land uses: $R = A \setminus B$

Because of the crop rotation that intensifies the farming land exploitation and balances the output of various different land uses (ex. orchards and vineyards, vegetable cultivation) the direct loss of agricultural surface area by the road construction, is classified in only three categories: arable land, land with permanent grass, and special cultivations. Generally, only higher quality soils are hold for arable land, while for grass and pastures lower quality soils are used.

The result of the intersection (common surface area) of the road corridor and the agricultural land is given in the form of a thematic map along with a table where the surface losses of agricultural land uses are depicted.

The remaining surfaces with agricultural land uses (existing agricultural surface areas minus the agricultural surface loss) is given in thematic map form, as well as in table of surfaces form so as to facilitate the further research of other impacts.

Negative (harmful) effect due to segmentation of the area surfaces means that the alignment of the new road not only requires farming land, but it also causes dissociation of several small agricultural surfaces from a continuous agricultural area. In such a way, parcels of small surface area result having at the same time non-favorable geometric shape (triangles with very sharp angles which are especially disadvantageous). These pieces of agricultural land lose their significance as farming areas completely, because their exploitation will not be any longer profitable. Due to segregation, these pieces are also considered as lost agricultural land surfaces.

Permanent degradation of agricultural production may be experienced as a consequence of frost [10]. The growth of agricultural products may also be affected by road traffic. The released gases from vehicles contaminate foods with contaminants that can be transferred through the food chain and accumulate. The effect of heavy metals accumulation due to road construction and function on plants and crops is similar to that of exhaust gases. [11]

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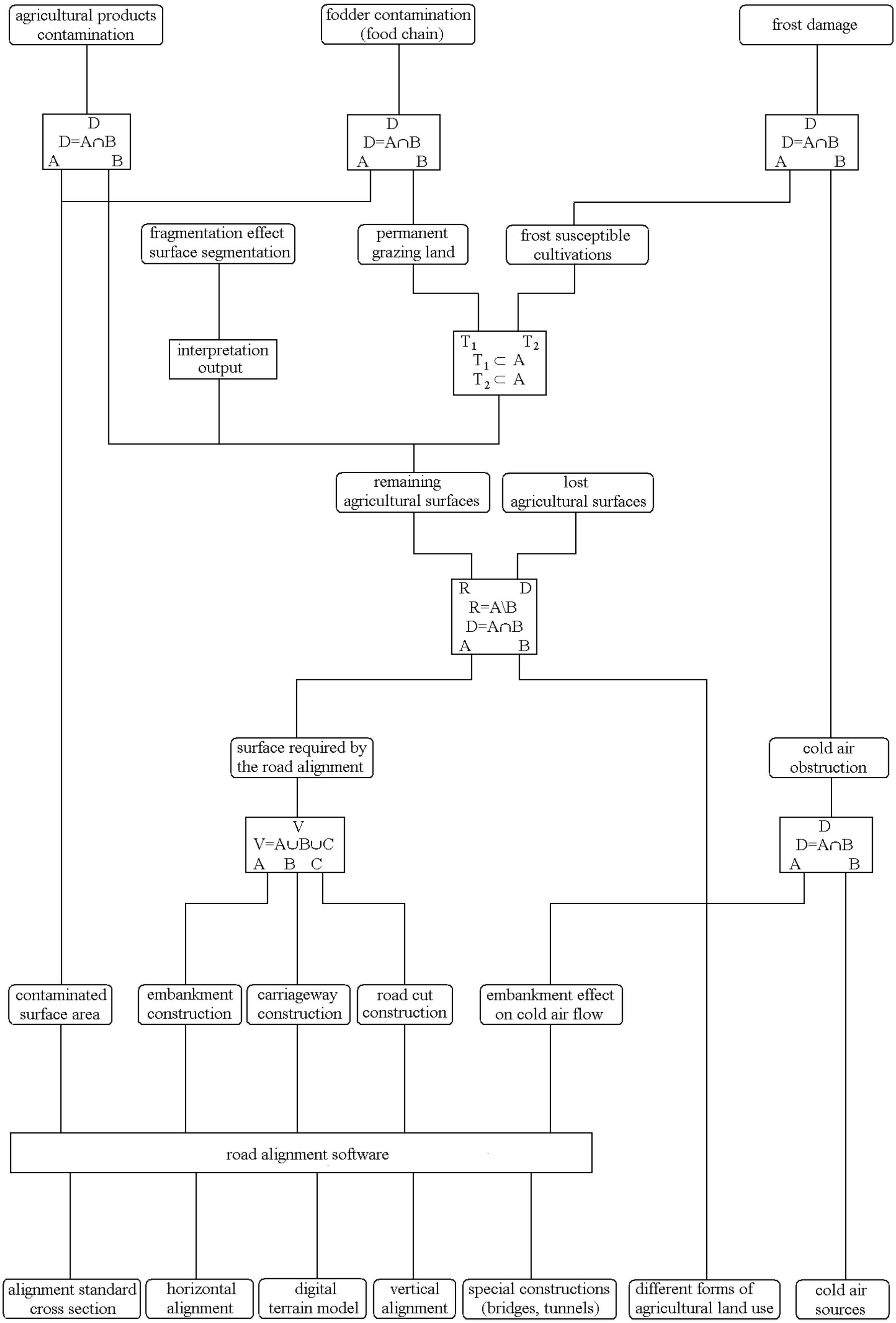


Figure 1. Flow chart of road alignment impacts on agricultural land uses

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3.1 Frost damage caused by cold air due to embankments

The microclimate can be greatly influenced by the construction of a road, such as the interruption of the cold air currents by the embankments. Kim et al. [8] investigated the effect of the height of embankments to prevent the cold air flow. The duration, frequency and extent of obstruction of the cold air flow are also dependent on several meteorological and topographical data. The road alignment program must be capable of calculating the surfaces "effect of embankments on cold air flow" (indication A in the flow diagram) based on distances (l) which depend on the height of embankments (suggested h:l = 1:5, with; h=height of the embankment and l=distance from the crest of the embankment, in which the accumulation of cold air extends).

Deep valleys with low wind speeds tend to produce very large quantities of cold air because they don't allow the mixing of low and high air layers, even during periods of wind or clouds.

Frost damage in the late spring or early fall affected by the blocking of cold air can reduce crop yields, especially that of thermophilic plants (e.g. orchards and vineyards) [12]. The cold air flow, as well as the cold air concentration can also have negative effects, depending on the kind of the affected land use [13].

If mounds (small hills) which are natural obstacles for cold air are opened and graded, they will free the cold air flow, which would be dangerous for crops relying on heat. The results will either be the reduction of the cultivation growth or destruction of cultivation.

The surfaces where damage due to frost is expected are gradually assessed.

- The intersection, D, of the surfaces "influence of embankments on the flow of cold air" (indication A in the flow diagram) with the surfaces "cold air sources" (indication B in the flowchart), i.e. $D=A\cap V$ gives the deteriorating surfaces due to "cold air flow obstruction".
- The intersection, D, of the surfaces "sensitive to frost crop cultivations" (i.e., orchards, vineyards, vegetable crop cultivations) selected from the "remaining agricultural land surfaces" (indication A in the flow diagram), with the degraded surfaces due to "cold of flow air obstruction" (previous result denoted with B in the flow chart), i.e. $D = A\cap B$ gives the surfaces of "frost damage due to the embankment".

3.2 Contamination of agricultural products and transfer through the food chain.

Near roads, the pollutants from the vehicle exhaust are diffused into the atmosphere and straddle in the form of sediments on the leaf surfaces. The larger part of the precipitate is washed by rain and is transferred to soil [14]. The green plants collect contaminants through their leaves and roots. Any accumulation of contaminants in the soil brings about harmful effects, especially in the plant generation following the first infected (i.e. crop cultivation cycle). The accumulation of contaminants will increase and they will pass on the food chain.

Contamination of pastures is considered as a special case. The grass that grows there is used as cattle feed over several years. In this way the pollutants can accumulate in the meat of cattle, which in the end reach a high degree of concentration that can be harmful to health [15].

The concentration of soil contamination is dangerous (either for agricultural products, or fodder) in a zone from the pavement edge having a width depending on traffic volume, speed and traffic composition, the wind speed and its direction relative to the road axis and the topographical factors. The alignment software calculates the risky areas, "contaminated surfaces", based on the traffic volume, or on the traffic volume and the wind direction (indication A in the flow diagram).

- The intersection, D, of "remaining agricultural surfaces" (indication B in the flow chart) with "contaminated surfaces", namely: $D = A\cap B$ gives the surface "Contaminated rural areas" where degradation of agricultural products is expected.
- The intersection, D, of "remaining meadow surfaces" (indication B in the flow chart) with "the contaminated surfaces", namely: $D = A\cap B$ gives the surface "contaminated pasture lands" which is separately presented as "animal feed contamination".

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4. CONCLUSIONS

A rural road network is under ambiguity owing to various reasons. The presence of the network and its traffic flows offer access possibilities and they contribute in the economic growth, while on the other hand they cause fragmentation.

Rural roads accelerate deforestation through the expansion of agricultural land and the increased commercial exploitation of resources. Intensified production may lead to soil degradation and erosion as well as pollution from fertilizers and pesticides. Poor road design may lead to flooding and other types of environmental damage.

The construction of artificial structures, such as road embankments, may cause changes in the temperature and airflows in an area thus leading to damages, reduced crop yields, or even a more general reduction of the quality of the land surrounding the road.

The effects of a rural road on its surroundings must be properly quantified in order to undertake effective mitigation measures aiming to enhance the reduction of fragmentation impacts. To achieve such a goal, several methods are available, either focusing on the road or on the traffic. The proposed system of software subroutines may assist engineers in selecting a rural road alignment which avoids the majority of negative impacts on the environment of the crossed areas. The software logic which is based on loss of contaminated surfaces gives a quantitative criterion to the road planning and design process.

References

[1] Simon, E., Braun, M., Vidic, A., Bogyó, D., Fábián, I., Tóthmérész, B. 2011. Pollution assessment based on elemental concentration of leaves tissue and foliage dust along an urbanization gradient in Vienna. *Environmental Pollution*, **159(5)**, 1229 – 1233.

[2] Main Roads, Western Australia, 2010. Handbook of environmental practice for road construction and maintenance works. Revised 2nd edition. Roadside Conservation Committee, Western Australia.

[3] Khodeir, L. M., Mohamed, A.H.M., 2015. Identifying the latest risk probabilities affecting construction projects in Egypt according to political and economic variables. From January 2011 to January 2013. *HBRC Journal*, **11(1)**, 129 – 135.

[4] Indian Road Congress (IRC), 2016. Rural road environmental management standard (environmental codes of practice).

[5] Jaarsma, C.F., Willems, G.P.A., 2002. Reducing habitat fragmentation by minor rural roads through traffic calming. *Landscape and Urban Planning*, **58,** 125 – 135.

[6] Jaarsma, C.F., van Langevelde, F., Beunen, R., 2013. Landscape ecology and rural roads: traffic calming for improving both landscape and wildlife? *Ekológia (Bratislava)*, **32(4)**, 352 – 360.

[7] Maletin, M., Tubić, V., Vidas, M., 2015. Functional classification of rural roads in Serbia. *International Journal for Traffic and Transport Engineering*, **5(2)**, 184 – 196.

[8] Kim, Y.M., You, K.P., You, J.Y., 2014. Characteristics of wind velocity and temperature change near an escarpment-shaped road embankment. *Scientific World Journal*, 13 p.

[9] Forman, R.T., 2006. Good and bad places for roads: effects of varying road and natural pattern on habitat loss, degradation, and fragmentation. *Proceedings of the 2005 International Conference on Ecology and Transportation*, (Eds. Irwin, C.L., Garrett, P., McDermott, K.P.) Center for Transportation and the Environment, North Carolina State University, Raleigh, NC, 164 – 174.

[10] Olesen, J.E., Bindi, M., 2002. Consequences of climate change for European agricultural productivity, land use and policy. *European Journal of Agronomy*, **16,** 239 – 262.

[11] Alyemeni, M.N., Almohisen, I.A.A., 2014. Traffic and industrial activities around Riyadh cause the accumulation of heavy metals in legumes: A case study. *Saudi Journal of Biological Sciences*, **21(2)**, 167 – 172.

[12] Anconelli, S., Facini, O., Marletto, V., Pitacco, A., Rossi, F., Zinoni, F., 2002. Micro-meteorological test of microsprinkers for frost protection of fruit orchards in Northern Italy. *Chemistry and Physics of the Earth*, **27(23-24)**, 1103 – 1107.

[13] Snyder R.L., deMelo-Abreu, J.P., 2005. Frost Protection: fundamentals, practice and economics. Volume 1. Food and Agriculture Organization of the United Nations, Rome.

[14] Janhäll, S., 2015. Review on urban vegetation and particle air pollution – Deposition and dispersion. *Atmospheric Environment*, **105**, 130 – 137.

[15] Madejón, P., Domínguez, M.T., Murillo, J.M., 2012. Pasture composition in a trace element-contaminated area: the particular case of Fe and Cd for grazing horses. *Environmental Monitoring and Assessment*, 184(4), 2031 – 2043.

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Environmental impact assessment of flood protection measure by Universal Matrix of Risk Analysis

M. Zeleňáková[*], L. Zvijakova

Department of Environmental Engineering, Technical University of Košice, 420 00 Košice, Slovakia
*Corresponding author: Email: martina.zelenakova@tuke.sk

Abstract

Introducing risk analysis in decision making on environmental impacts of actions in water management can be a decisive issue for the design of project alternatives. This paper explores the benefits of using the risk assessment/analysis technique in the evaluation of FMM by examining the results of the EIA for a selected planned FMM in Slovakia. The aim is to improve transparency and minimize subjectivity in the EIA process specifically in the projects of FMM proposal. This methodology is intended to streamline the process of environmental impact assessment of constructions in the field of the water management. It is expected that EIA will continue to act as an effective tool to prevent the application of investments in Slovakia which by their degree of environmental damage many times outweigh their benefits. In some cases, EIA is understood only as a "mirror" to comply with legal or technical standards, which is not sufficient for modern environmental planning. The assessment process should take into account the emotions and feelings of the public, stress factors, fear of risk and criteria reducing the quality of life. Generally, we can say that impact assessment in Slovakia is still based on professional principles, as is evidenced by EIA documentation on a standard or even high level. The weaknesses of the EIA process lie in the methods used within EIAs. The challenge for environmental research is to improve the guidance provided for impact analyses so as to encourage good practice within EIAs, and to eventually strengthen the consideration of environmental issues in the decision-making concerning new projects. To this end, the application of risk analysis to EIA has been chosen as the subject of this research. The work points out the possibility of improving existing methods of assessing the impacts of proposed activities by applying risk analysis in assessing the impact of water structures on the environment. Utilizing the methods of risk analysis to assess the impact of activities on the environment and human health is an original proposal.

Keywords: environmental impact assessment (EIA); flood protection; risk analysis (RA); decision making

1. INTRODUCTION

In the European Region, floods are the most common disasters, causing extensive damage and disruption. Flood mitigation measures are being undertaken throughout the centuries to reduce flood damages and losses. Experience with the implementation of the Law on Environmental Impact Assessment confirmed that the technical and urban development of country must go hand in hand from the beginning with knowledge of how much influence new activity will have in a particular area, and how potential negative impact on the environment will be minimized [1,2].

The environmental effects of development can be difficult to predict. Predictions must often be made when there is still uncertainty about outcomes, be they negative or positive. Because EIA is a predictive tool it deals with uncertainty and risk. EIA is information and knowledge dependent -

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knowledge about environmental values that may be at risk from proposed development, knowledge about the nature, extent and duration of risks to which those environmental values may be exposed, knowledge about what can be done to prevent, avoid or mitigate those risks and identify opportunities, and knowledge about whether those identified risks were indeed controlled. It is tension about how much information and knowledge is necessary to have confidence in predictions about impacts that is at the heart of EIA [3]. Risk assessment and EIA are similar in concept as they both deal with the prediction of the future impacts or consequences arising from proposals and uncertainties about the exact nature, probability, frequency and magnitude of impact or consequences. Both seek to inform the decision making process about the significance of detrimental impacts and the appropriateness of risk treatments or mitigation measures. The European Union has encouraged its members to apply risk assessment in EIA, particularly to extreme events but very little specific guidance is available on how to apply risk assessment in EIA [4].

The paper introduces the environmental impact assessment process in Slovakia and involvement of risk analysis in environmental impact assessment. Risk analysis is an appropriate tool to determine the level of the risk of the proposed flood mitigation measures and through which it is possible to choose the alternative with the lowest level of risk for the environment. The objective of the paper is to propose a methodology for assessing environmental impact of flood protection objects. It offers some recommendations and conclusions with the aim of providing valuable insights for decision makers, planners and policy makers for the improvement of the EIA practice.

2. MATERIALS AND METHODS

2.1 Establishing the context

The proposed methodology is as follows.

- ***Characteristics of the current state of the environment in the affected area***

As the primary step it is important to know the characteristics of the current state of the environment.

- ***Explanation of the reasons why the proposed activity is required in the locality***

It is necessary to increase the flood protection of the inhabitants and environment in the village. Increasing the flood protection can be achieved by various measures, ranging from less effective measures of increasing the retention capacity and erosion control of the landscape to highly effective technical flood protection objects. The purpose of the proposed action – flood protection measure – is regulation of drainage conditions in order to improve flood protection.

- **Brief description of alternatives of the proposed activity A_j (A_0, A_I, A_{II})**

Consideration of potential alternatives in the EIA process is one of the most critical elements of the scoping phase. Its importance is highlighted by [5] and by the Council of Environmental Quality in the United States, which describes the consideration of alternatives as the ‘heart’ of EIA [6]. By implication, alternatives are essential to the EIA process, yet they are often inadequately handled. It is not uncommon to find that feasible alternatives are omitted deliberately or that alternatives proposed by stakeholders are rejected without adequate justification. Consideration of alternatives is one of the most critical elements of the environmental assessment process. Its role is to provide a framework for sound decision-making based on the principles of sustainable development.

2.2 Identification of impacts

The aim of this step for the purposes of impact assessment of the proposed activity on the environment is to identify sources of risk areas and their impact on the various components of the environment, including inhabitants. The proposed identification of the environmental impacts of stressors is based on the modified method of risk analysis – UMRA (universal matrix of risk analysis).

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- ***Identification of sources of risk - stressors***

Potential stressors associated with the proposed activities in the field of water management have been systematically identified through a series of studied references, consultation with experts and expert estimation. The main objective of this task was to identify pollutants or activities that may alter the natural environment as a result of the planned activities. Designated stressors associated with the above-mentioned issues are proposed in Figure 3.

- ***Definition of areas of impact***

In accordance with established practice of EIA, the impact of stressors is assessed and subsequent risk analysis is carried out for these environmental components: population, rocks and minerals, geodynamic phenomena and geomorphological conditions, climatic conditions, air and water conditions, soil, flora, fauna and their habitats; country - the structure and land use, landscape character, protected areas and their buffer zones; territorial system of ecological stability; urban environment and land use, cultural and historical heritage, cultural and historical values, archaeological and paleontological sites and important geological sites and other effects.

- ***Identification of the environmental impacts of stressors using UMRA***

One approach to identify potential risks to the environment (stressor effects on components of the environment) is to use a template for UMRA of the proposed activities related to water management, which is proposed in Figure 1. Records are made by marking the box in which the potential risk occurs and then through detailed characteristics.

3. RESULTS AND DISCUSSION

The risk analysis according to the proposed methodology consists of three activities: identification, prediction and evaluation of impacts.

3.1 Prediction of impacts

Prediction of impacts is based on the fact that there is a relationship between the proposed activity and the environment. These relationships can be described as a string of probabilities and consequences of stressor on environmental components.

To predict effects it is necessary to propose a set of criteria that reflect the impact of each proposed activity on the environment.

- ***Determination of probabilities***

Probability is expressed as the possibility of adverse effects from exposure to stressors on environmental components. To determine the value of the probability "P_i" of adverse effects as a result of exposure to the stressors impacts on various components of the environment, four levels of probability were chosen as shown in Figure 1.

- ***Determination of consequences***

Impact occurs after exposure to a negative stressor on the individual components of the environment. The consequences of the adverse impact of the stressor must be examined at different levels. For example, damage to human health is usually considered at the individual level, but environmental damage is usually considered at the level of populations, species or communities. Four levels of stressor exposure to various components of the environment were chosen for determining the value of the consequence of “C_i", as shown in Figure 1.

Four levels of probability and consequence were proposed based on the literature studied, such as by [7] or [8].

The assessment of consequence defines a negative impact. For qualitative risk assessment impact is frequently expressed in the following terms: negligible, low, medium or high.

In Figure 3 is a schematic representation of processing of stressors that have impacts on components of the environment during the activity – construction of flood protection object. All

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stressors and their brief description are listed in the Catalogue of Stressors, as well as a schematic example of the determination of indicators and criteria for the probabilities and the consequences. The Catalogue of Stressors was created based on the authors' proposal, and it reflects consultations with experts and professionals in the field of water management and environment protection.

Based on the proposed Catalogue of Stressors [1], for each of the assessed variants of the proposed activity of flood protection the probability P_i and consequence C_i is stated as is expressed in Figure 1.

3.2 Evaluation of impacts

Evaluation of potential impacts of the activity on the environment is the most important step in the EIA process. The aim is to define which environmental changes may result from the proposed activity and to assess the significance of these changes. For the purpose of the proposed action assessment, it is important to determine the level of risk which arises from the action of each stressor on the individual components of the environment as a consequence of the activity.

- ***Calculation of risk R_i***

For evaluation of impacts the calculation of individual risk R_i is required, which is done using the following equation (1):

$$Ri = P_i \times C_i \qquad (1)$$

where

R_i is individual risk of each stressor impact on the component of the environment,

P_i is probability,

C_i is consequence.

Risks R_i are calculated individually for each stressor which has an impact on the components of the environment for each considered variant for determination of risk index IR_j.

- ***Characteristics and estimation of the level of individual risks***

In its simplest qualitative form, is possible the relationship between risk and its parameters illustrated using a simple matrix (see Figure 1.). With the increasing level of risk (hazard ratio) increases the risk significance.

A similar approach uses the semi-quantitative analytical tool. The calculated risk of each individual risk is then classified into one of the matrices of risk analysis, and thus the level of risk is estimated.

The objective of this risk matrix is to provide guidance to characterize the relationship between probabilities and consequences of individual risks. Assessments of probability and consequence are combined in order to set the risk of individual stressors to environmental components. The risk matrix is a tool for obtaining a risk assessment of the proposed activity on the environment.

4. CONCLUSIONS

Environmental quality is the condition for the existence of everyone's life. Its developments are affected by all of its natural compounds and ecosystems. Their status is currently changing not only on local and regional but on a global scale as well. We may say that the quality of the environment is improving thanks to the environmental infrastructure. These include also the construction of flood mitigation measures in existing or potential flood risk areas, also in Slovakia.

Risk analysis is a formal methodology to marry up available technical information and stakeholder values to support decision making in many fields, and can be especially valuable in environmental decision making.

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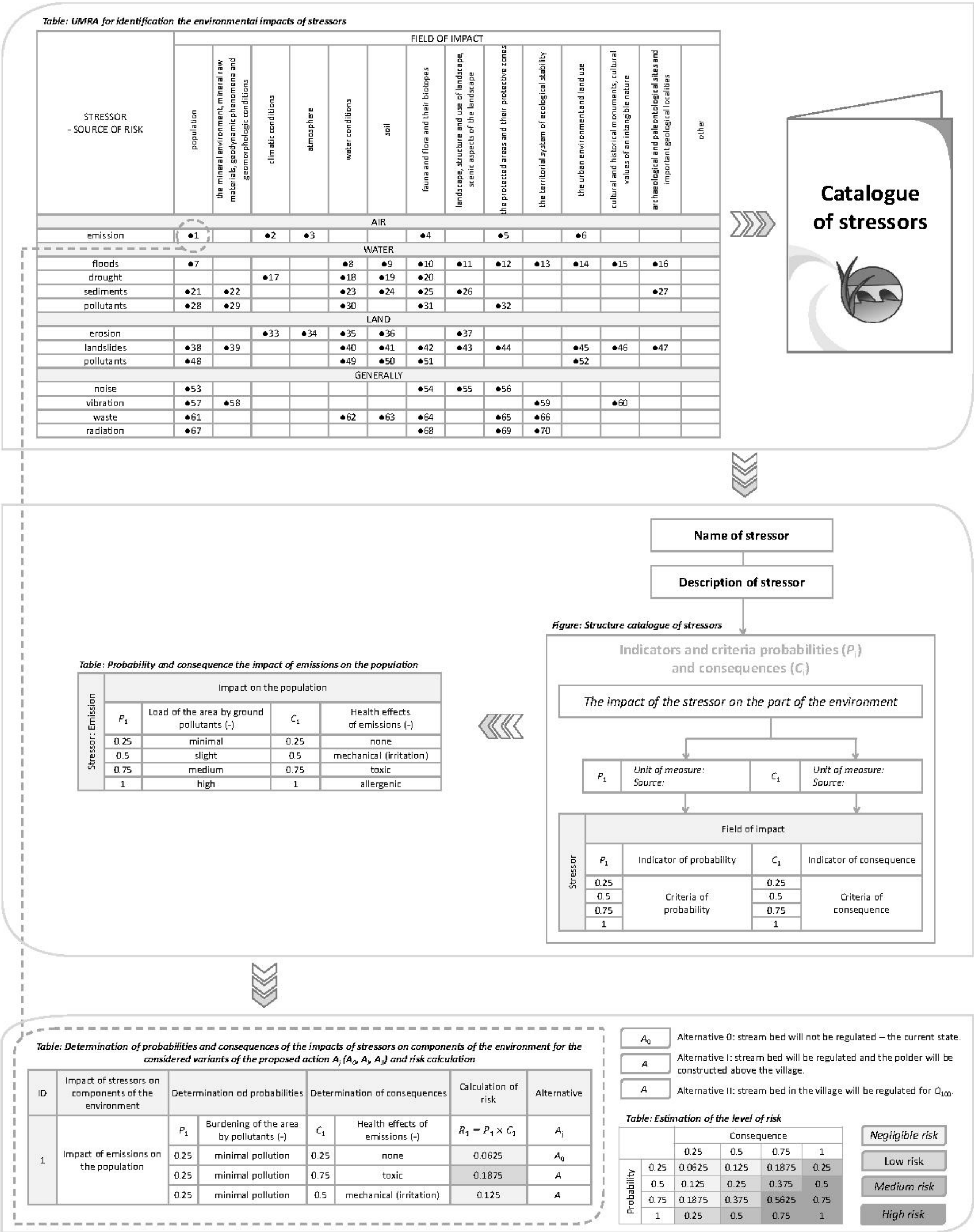


Figure 3. Structure methodology part of B stage: risk analysis and examples application part

A risk-based approach has the potential for a number of advantages including (EPA, 2009):

- greater transparency in decision-making processes;
- support for informed, consistent and defensible decision-making;

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- consistent with the precautionary principle;
- more systematic approach to evaluating the magnitude of environmental impacts
- prioritises the environmental impacts of concern, the application of management and controls and the focus of audit programmes;
- improves environmental accountability of proponents;
- provides an effective basis for the engagement of key stakeholders to influence environmental outcomes;
- provides a sound basis for the development of targeted research and development programmes.

Risk-based approaches should be used to inform key stages of the environmental impact assessment process:

- scoping of the proposal at or following referral,
- evaluation of impacts and design of mitigation measures by the proponent,
- assessment of impacts arising from the proposal,
- assessment of proposed mitigation measures.

Within each of these phases, risk analyses and evaluations of environmental risks should be conducted at an increasing level of detail as a proposal proceeds through the process.

Introducing risk analysis in decision making on environmental impacts of actions in water management can be a decisive issue for the design of project alternatives.

Currently, the identification of key issues, the determination of the acceptability of impacts and the appropriate management response according to a scale of impact in the EIA process is not systematic, consistent or transparent in most instances. The current process rightly involves judgements on these matters but they are not always well documented or transparent. Risk assessment in EIA has often been restricted to human health and safety risk assessments with little application to ecosystem impacts. The risk-based approach provides systematic consideration of the probabilities and significance of potential environmental impacts and a transparent approach to addressing these matters. Depending on how it is applied, it can also provide an opportunity for stakeholders and regulators to participate in the process to determine levels of impact significance, acceptability and mitigation (EPA, 2009).

Acknowledgement

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References

[1] Zvijáková, L., Zeleňáková, M, 2015. *Risk analysis in the process of environmental impact assessment of flood protection objects* (in Slovak). Praha: Leges, 255 p.

[2] Zvijáková, L., Zeleňáková, M., Purcz, P. 2014. Evaluation of environmental impact assessment effectiveness in Slovakia. *Impact Assessment and Project Appraisal*. **32 (2)**, 150-161.

[3] Lexer, W., Paluchova, K., Schwarzl, B. 2006. *Risk Assessment. IMProving the IMPlementation of Environmental IMPact Assessment*, „(IMP)3“. Risk Assessment D 3.2 Report WP 3. Vienna: Österreichisches Institut für Raumplanung.

[4] EPA (Environmental Protection Authority). 2009. *Review of the Environmental Impact Assessment Process in Western Australia*. Perth, Western Australia: EPA.

[5] Glasson, J., Therivel, R., Chadwick, A. 1999. *Introduction to Environmental Impact Assessment*, UCL Press.

[6] Magness, T.H. 1984. NEPA, the regulations of the US Council on Environmental Quality and the heart of EIA. In *Proceedings of the Paper Presented to the Dutch-US Seminar on Environ-mental Management*. Washington DC.

[7] Australian Government. 2005. *Risk Analysis Framework. Australia*. Commonwealth of Australia.

[8] Department of Defense. 2000. MIL-STD-882D *Standard practice for system safety*. USA: Department of Defense.

Assessment of the natural and anthropogenic sources of chemical elements around a Zn-Pb mine: Distribution of geochemical fractions

D. G. Megadouka[1], D. L. Bouranis[2], K. G. Serelis[1*]

[1]Department of Natural Resources Management & Agricultural Engineering, Agricultural University of Athens, 118 55, Athens, Greece.
[2]Department of Crop Science, Agricultural University of Athens, 11855, Athens, Greece.
*Corresponding author: Email: serelis@aua.gr

Abstract

To evaluate the heavy metal contamination and investigate the sources ofCd, Pb, Cr, Co, Zn and N in soils around a Pb-Zn mine at Lavrion peninsula, Attiki, Greece, 45 representative soil samples were collected from two depths (A: topsoil and B: subsoil). Metal fractionation was obtained following a 4-step sequential extraction scheme and the following fractions were collected for each sample: the acid soluble (1st), the reducible (2nd), the oxidisable (3rd), and the residual (4th) one. All soil samples contained elevated concentrations of Cd, Pb and Zn. Cr (~85%), Ni (~70%) and Zn (~52%) were mainly found at 4th fraction. Pb (~64%) and Cd (~40%) were found at the 2nd fraction, Co was found at 2nd (A: 34%) and 4th fraction (B: 31%). Multivariate analysis suggested that Zn, Cd and Pb originated from anthropogenic sources, mostly as a result of historical Zn and Pb mining and smelting, while Co, Ni, and Cr were associated with parent rock and therefore had natural sources

Keywords: anthropogenic contamination; heavy metals; sequential extraction; mining; Lavrion

1. INTRODUCTION

The accumulation of metals in soils may be of natural origin or related to human activity. Many recent studies have focused on the characterisation of metal contamination in soils near to metallurgical industrial sites, whether previously or currently active [1,2]. Anthropogenic activities, such as mining and smelting of metal ores, have increased the prevalence and occurrence of heavy metal contamination at the Earth’s surface [3]. Knowledge of metal partitioning in soils, allows better understanding of metal behavior as opposed to studies of total metal concentrations, which provide limited information on the mobility and bioavailability of the metals of interest. Sequential chemical extractions are based on a series of successively aggressive reagents to extract metals associated with specific fractions of soils [4,5,6,7], thus allowing discrimination among the different sources of element concentrations in samples. The objectives of this research were (i) to determine the chemical partitioning of Pb, Zn, Cd, Co, Cr and Ni using a modified BCR sequential extraction procedure, (ii) to determine the source of the metals in the area surrounding the mine, and (iii) to assess and evaluate the environmental risk associated with heavy metal pollution in soils from the studied area.

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2. MATERIALS AND METHODS

2.1 Study area

Lavrion is located in the southeastern part of Attica, about 60 kilometers from Athens, Greece and is known worldwide as one of the oldest mines. Ancient Greeks exploited Lavrion ores from 3500 BC, to produce mainly silver and lead. The primary ore of Lavrion peninsula comprises of two groups: an iron–manganese ore which is generally limited, and mixed sulphides ores which were intensively exploited, characterized by the presence of galena (PbS) rich in silver, sphalerite (ZnS) and pyrite (FeS_2). The revival of mining and smelting activities at Lavrion took place in 1860, when ancient mining areas were brought to light and the use of slag was proposed. Until 1989, where these activities were officially stopped, the extensive exploitation of mineral ores resulted in high contamination of the area with heavy metals.

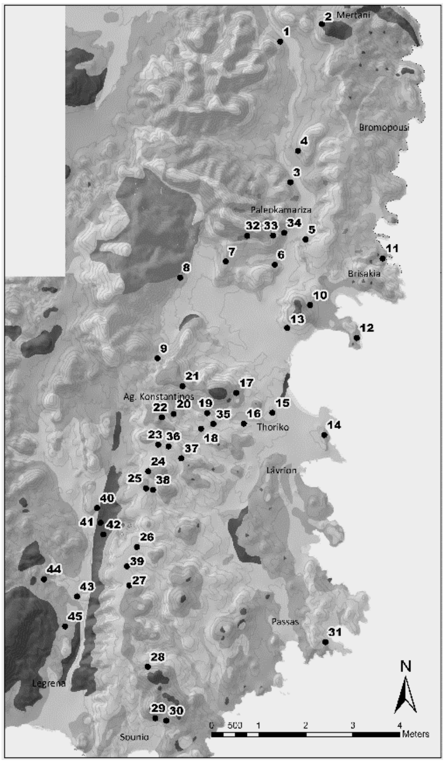


Figure 1. Location of sampling points on Lavrion peninsula

2.2 Soil sampling and analytical methods

Soil samples from 45 sites of Lavrion peninsula (Figure 1) were taken from two depths: topsoil (0 - 10 cm; A) and subsoil (10 - 30 cm; B). In the laboratory, all samples were air dried and sieved to pass through a 2mm mesh. The physicochemical properties of the soil samples were determined by means of standard methods. PH and Eh were determined, organic matter content by the Walkley–Black method, $CaCO_3$ content using a Bernard calcimeter [8] while particle-size distribution was based on Stokes' Law standard procedure. For the fractionation of heavy metals an optimised BCR procedure was followed (Table 1) [9]. Each extraction step was performed in triplicate, starting with 1 g of sample. All reagents were of analytical grade quality. Concentrations were determined using Atomic Absorption Spectroscopy.

Table 1. Reagents and conditions employed for the modified BCR sequential extraction procedure.

Step	Fraction	Reagent & conditions
1	Acid extractable	1 g of air-dried soil + 40mL 0.11 mol L^{-1} CH_3COOH, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. The residue was washed by adding 20 ml of distilled water, shaken for 15 min & centrifuged for 20 min at 3000 rpm.
2	Reducible	Residue + 40mL 0.5 mol L^{-1} NH_2OH-HCl, pH=1.5, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. Residue washing as in step 1
3	Oxidisable	Residue digested with 10mL 8.8 mol L^{-1} H_2O_2, 1 h at room temperature, 1 h at 85 ^oC in a water bath and reduced to 2-3 mL. Then 10 mL 8.8 mol L^{-1} H_2O_2 added, 1 h at 85 ^oC in a water bath and reduced to 2-3 mL, 50 mL of 1 mol L^{-1} NH_4COOCH_3 was further added, shaken 16 h at room temperature, centrifuged at 3000 rpm for 20 min. Residue washing as in step 1.
4	Residual	Residue + 7 mL 12 mol L^{-1} HCl, 2.3 mL 16 mol L^{-1} HNO_3, 16 h at room temperature, 2 h gentle reflux, cool, filtered through Whatman 540.

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2.3 Statistical analysis

Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA) are powerful tools for segregating sources contributing to observed pollution [10,11]. FA was performed by evaluation of principal components and computing the eigenvectors higher than 1 (Kaiser Criterion). Afterwards, Varimax rotation was applied because orthogonal rotation minimizes the number of variables with a high loading on each component and facilitates the interpretation of results. In this case, the result of the KMO and Bartlett test suggested that PCA was suitable for analysis of the data set. Correlation matrix (CM) was used to identify the relationship between heavy metal contents.

HCA was applied to identify different geochemical groups, clustering the samples with a similar heavy metal content. Ward's algorithmic method of agglomeration and squared Euclidean distance as the measurement of similarity were used. Results are shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters are represented [12]. Correlations between parameters, FA and HCA were applied using SPSS 11.0 statistical computer program.

3. RESULTS AND DISCUSSION

3.1 Soil properties

At 40 samples out of 45 collected from depth A, the pH was found to range from 7.4-8.2 reflecting alkaline conditions. Eh ranged from 167-320 mV, suggesting aerobic conditions, in which the metals are usually in the form of cations. Organic matter content ranged from 1.7-13.7%, while $CaCO_3$ content ranged from 0.2-39.5%. The majority of samples at depth A presented sandy-loam soil texture. Regarding physicochemical properties of depth B, pH ranged from 6.6-8.3 with 43 samples to be characterized by alkaline conditions; Eh conditions were the same as in depth A and organic matter ranged from 0.6-9.7%. $CaCO_3$ content ranged from 0.1-42.6%. The majority of the samples at depth B presented sandy-loam and sandy-clay-loam soil texture.

3.2 Geochemical forms of metals in soil

Ni - At depth A the majority of the Ni was in the residual soil fraction with 69% of the total, probably because it exists in the silicates. According to Sposito [13], this may happen because of the presence of Ni as isomorphous substitutions of Fe and Al in the spinel group of minerals or as inclusions in silicate networks of smectite and illite. It should be noted that Anju and Banerjee [14] at Rajasthan, India and Forghani et al [15] at Central Iran have also pointed the presence of Ni in the residual phase of soils from Pb–Zn mining districts. The reducible and the oxidisable fraction represented 14% and 13% of the total content, respectively. The acid exchangeable fraction adsorbed only the 4% of the total. Similar metal distribution at the four different fractions was found at depth B (4^{th}: 71%, 2^{nd}: 15%, 3^{rd}: 10% 1^{st}: 4%). According to the geology of the area, the presence of ophiolites and mafic parts of the shales of the parent rock may be responsible for the Ni concentrations. Also, Ni exists to ZnS, PbS [16]. Total concentrations Ni at depth A and B ranged from 8.0– 646.9 mg kg^{-1} and 31.1– 539.7 mg kg^{-1} respectively.

Cr - A significant fraction of Cr was linked to the residual soil fraction, reaching 86% and 85% at each depth. Similar results have shown that Cr is mainly present in the residual phase of soils, because Cr^{3+} replaces $Fe^{3+}$and Al^{3+}in silicate minerals, especially clays [17]. The rest of the fractions at both depths varied from 4% to 5% of the total at each fraction. Like Ni, Cr is also indicated to have geogenic origin. Total concentrations of Cr at depth A and B ranged from 13.7 – 242.1 mg kg^{-1} and 15.8– 267.2 mg kg^{-1} respectively.

Co - At depth A, Co was adsorbed in both the reducible (34%) and the residual (31%) fraction. This may be explained by the strong affinity of Co with Mn-oxides [18,19]. The oxidisable fraction followed with 22% and the acid extractable with 11%. At depth B, Co was also absorbed mainly in

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the reducible (30%) and in the residual (31%) fraction, while the percentage of the oxidisable fraction increased to 26% of the total. The acid extractable represented the 12% of the total Co at depth B. The major ore deposits of Co occur as sulfides [20]. Therefore, the mineralization of mixed sulphides of the region explains the presence of Co. Total concentrations of Co at depth A and B ranged from Non-Detectable (ND) values to 45.8 mg kg^{-1} and ND to 60.9 mg kg^{-1} respectively.

Zn - Like Ni and Cr, most of the Zn was associated with the residual fraction of the soils, ranging from 50% - 54% at each depth. The reducible fraction absorbed the 28% and 24% of the total Zn at each depth, due to its affinity to oxy-hydroxides, especially in alkaline conditions [21], as in studied soils. At depth A, the acid extractable fraction represented the 12% and the oxidisable fraction the 10% of total Zn. As regards the distribution of fractions in depth B, the 1^{st} and 3^{rd} fraction were similar as in depth A, with mean percentages up to 10% and 12% respectively. Sphalerite (ZnS) is a sulphide ore in which Zn content can reach up to 67.1 % and is widely present in Lavrion peninsula. Total concentrations of Zn at depths A and B ranged from 69.0 - 38100.5 mg kg^{-1} and 58.4 - 55031 mg kg^{-1} respectively.

Cd - The highest content of Cd was associated with the reducible fraction, at depth A 41% and at depth B 38%. Cd was also present in significant amounts in acid extractable fraction, representing the 36% of the total at both depths. In a similar study, at Mae Sot District area in Thailand where a Zn mine was operated for over three decades, it was found 100.9 mg kg^{-1} of Cd in acid extractable fraction of BCR, while at reducible fraction Cd reached 114.9 mg kg^{-1} [22]. In soils whose pH is greater than 7.5 (the studied soils pH ranged between 6.5 - 8.3), Fe hydroxides are suitable sites for absorption of Cd [23]. The oxidisable and the residual fraction represented at depth A the 10% and 13% and at depth B the 13% and 12% of the total Cd, respectively. The amount of total Cd ranged from 1.9 to 194.1 mg kg^{-1} at depth A and from 0.3 - 219.2 mg kg^{-1} at depth B. Therefore, significant Cd concentrations are expected, because Cd is obtained as by-product of smelting of ZnS, in which it has been substituted for some of Zn and no ores are used primarily as source of Cd [24].

Pb - Most of Pb amount was associated with the reducible fraction of the soils, representing the 63% at depth A and the 65% at depth B of the total; this finding is in agreement with the results of similar studies on mining and smelting areas [25,26]. Fe-Mn oxy-hydroxides are important scavengers of metals in soils, particularly at pH > 7 [27] as in the studied soils. Pb was also present in the oxidisable fraction with 19% and 17% of the total extracted, at depth A and B respectively. The amount extracted from residual fraction represented the 14% and 16% at each depth, may be due to PbS that is present at the parent rock. The proportion of Pb related to acid extractable fraction was not significant and reached 5% of the total extracted in both depths. Total concentration at depth A ranged from 65.2 to 41606.9 mg kg^{-1} and at depth B from 87.2 to 99812.7 mg kg^{-1}.

Table 2. Metal concentrations (mg kg^{-1}) in each fraction of modified BCR in soil samples at two depths

	Acid extractable	Reducible	Oxidisable	Residual
NiA	ND – 34.9	ND – 104.0	ND – 48.8	3.3 – 500.1
NiB	ND – 23.8	ND – 115.1	ND – 51.7	20.5 – 357.3
CrA	ND - 13.6	ND – 19.8	1.0 – 18.8	7.9 – 208.5
CrB	ND – 13.5	0.3 – 13.4	1.2 – 30.1	12.8 – 245.9
CoA	ND – 11.3	ND – 28.5	ND – 27	ND – 29.6
CoB	ND – 16.8	ND – 29.6	ND – 30.2	ND – 30.7
ZnA	ND - 13560	8 - 31920	4.7 - 3620	54 - 4659
ZnB	ND - 17040	0.7 - 17040	2.9 - 19800	42.7 - 4584
CdA	ND - 77.7	ND - 60.2	ND - 46.9	ND - 17.0
CdB	ND - 112	ND - 54.0	ND - 41.5	ND - 28.1
PbA	ND - 4518.4	10.8 - 22820	ND - 9390.5	ND - 4132.5
PbB	ND - 11000	30.7 - 37352	ND - 46370	ND - 5090.7

3.3 Assessment of potential environmental risk

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In order to estimate the environmental risk associated with heavy metal pollution in the study area, the soil samples were classified according to a risk assessment code (RAC) [28] (table 3). RAC is defined as the percentage, of the ratio of the FI fraction (metal associated with exchangeable and carbonate fraction) to the total concentration of elements in the soil and a risk scale based on RAC has been proposed by Rodríguez et al. (2009) [28].

3.4 Factor analysis

Topsoil - The correlation matrix between the total contents of six heavy metals in 45 samples is reported in Table 4. Zn is correlated with Cd (loading 0.798) and with Pb (loading 0.723). Also Cd is correlated with Pb (loading 0.777) and a weak correlation exist between Ni and Cr (0.559).

FA was used to identify the factors that affect the presence of heavy metals in soil. FA for the depth A exported three factors (Table 5). The first factor (F1), explaining 45.1% of total variance, defined Zn (0.917), Cd (0.925) and Pb (0.897) as positively related. It is suggested that these three elements were affected by anthropologic activities. The second factor (F2), explaining 23.2% of total variance, revealed a group with high positive loading composed by Ni (0.888) and Cr (0.865). Third factor (F3), which describes 16.7% of variance, represented a high positive factor loading of 0.995.

Table 3. The result of risk assessment code for soil samples of the study area.

	No risk <1% RAC	Low risk 1-10% RAC	Medium risk 11-30% RAC	High risk 31-50% RAC	Very high risk >50% RAC
NiA	8	25	4	-	-
NiB	9	27	5	-	-
CrA	3	15	-	-	-
CrB	1	15	1	-	-
CoA	-	-	-	-	-
CoB	-	-	-	-	-
ZnA	1	23	14	3	1
ZnB	1	15	12	10	-
CdA	1	2	11	25	2
CdB	-	1	15	19	3
PbA	4	32	-	4	-
PbB	3	33	-	3	-

Table 4. Correlation matrix between heavy metals of the collected samples of topsoil.

	ZnA	CdA	PbA	CoA	NiA	CrA
ZnA	1.000					
CdA	**0.798**	1.000				
PbA	**0.723**	**0.777**	1.000			
CoA	-0.015	0.059	0.070	1.000		
NiA	0.083	0.173	0.150	0.076	1.000	
CrA	0.219	0.235	0.218	-0.008	**0.559**	1.000

The dominated by Zn, Cd and Pb F1 explains the greatest amount of variance and is interpreted by ancient and recent extensive mining and smelting that prevailed in the region. Mining and smelting of galena (PbS) and sphalerite (ZnS) resulted in the intense presence of Pb and Zn. Also the association between Cd and Zn is expected, as demonstrated in correlation matrix table (Table 4); Cd is obtained as by-product of the smelting of ZnS, in which it substitutes for some of Zn [22]

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Table 5. Factor loadings of each variable, variance, explained and cumulate variance of the principal components of topsoil. Values in bold represent factor loadings values higher than 0.5

element	F1	F2	F3
ZnA	**0.917**	0.059	-0.057
CdA	**0.925**	0.127	0.040
PbA	**0.897**	0.106	0.062
CoA	0.025	0.020	**0.995**
NiA	0.040	**0.888**	0.091
CrA	0.165	**0.865**	-0.066
Variance %	*45.1*	*23.2*	*16.7*
Cumulative %		*85.2*	

because Cd is closely related with Zn in its geochemistry; both elements have similar ionic structures and electronegativities. Therefore, F1 refers to metals involved exclusively in the mining and smelting at Lavrion peninsula and can be defined as an anthropogenic component. F2 includes Ni and Cr, and could be considered as a natural component, because the presence of these heavy metals is related to ophiolites and to the mafic parts of the shales of the parent rock of the area. F3 explains only the presence of Co at depth A. This probably occurs due to the heterogeneous distribution of Co in the soil at depth A. As discussed in the geochemical analysis, it is not clear in which fraction Co is concentrated, since reducible fraction absorbed 34% of total Co and the residual one 32%. To identify the possible interpretation of this factor, further statistical analysis with Hierarchical Cluster Analysis tool was conducted as it follows.

Subsoil – The correlation matrix between the six heavy metals for depth B is reported in Table 6. The pairs of metals presented were the same as for the depth A, but with higher loadings reflecting stronger correlations.

Table 6. Correlation matrix between heavy metals of the collected samples of subsoil.

	ZnB	CdB	PbB	CoB	NiB	CrB
ZnB	1.000					
CdB	**0.959**	1.000				
PbB	**0.828**	**0.839**	1.000			
CoB	0.157	0.105	-0.031	1.000		
NiB	-0.026	-0.068	-0.029	0.429	1.000	
CrB	0.164	0.072	0.095	0.419	**0.616**	1.000

FA for the depth B exported two factors interpreting the 79.2% of the total variance of the variables (Table 6). Thus, F1 explained 46.5% of the total variance and is dominated by Zn, Cd and Pb with factor loadings 0.970, 0.975 and 0.924, respectively. F2 explained 32.7% of the total variance and is dominated by Co, Ni and Cr with factor loadings 0.734, 0.854 and 0.844, respectively. Consequently, it seems that the metal associations at depth B were more defined, especially for lithogenic metals. More specifically, F1 was composed by the same metals as in depth A, suggesting their anthropogenic source. However, F2 at depth B included Co along with Ni and Cr and probably suggests their lithogenic origin.

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Table 7. Factor loadings of each variable, variance, explained and cumulate variance of the principal components of subsoil. Values in bold represent factor loadings values higher than 0.5.

element	F1	F2
ZnB	**0.970**	0.094
CdB	**0.975**	0.015
PbB	**0.924**	-0.012
CoB	0.067	**0.734**
NiB	-0.089	**0.854**
CrB	0.093	**0.844**
Variance%	*46.5*	*32.7*
Cumulative %	*79.2*	

3.5 Cluster analysis

Topsoil - HCA was applied in order to confirm FA results. Two main groups were displayed for the depth A (Figure 2). The first group included the strongest cluster Zn-Cd, while Pb was related into this branch afterwards, implying perhaps a common source. The second group included a cluster of Ni-Cr, while Co is weakly related with the latter cluster (a long distance was recorded).

Regarding results of HCA for depth B, Figure 3 presents the association between groups of variables. The first group concerning the anthropogenic elements, included the same association as in depth A. The only difference between the two depths was the shorter distance of Co where joins the second group.

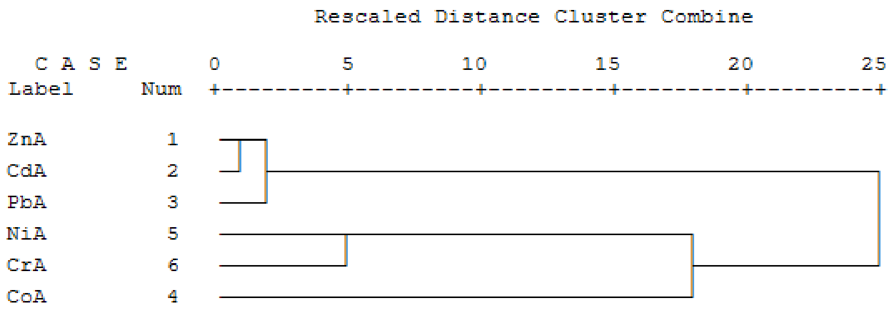


Figure 2. Dendrogram derived from the HCA of heavy metals content in analyzed soils at depth A.

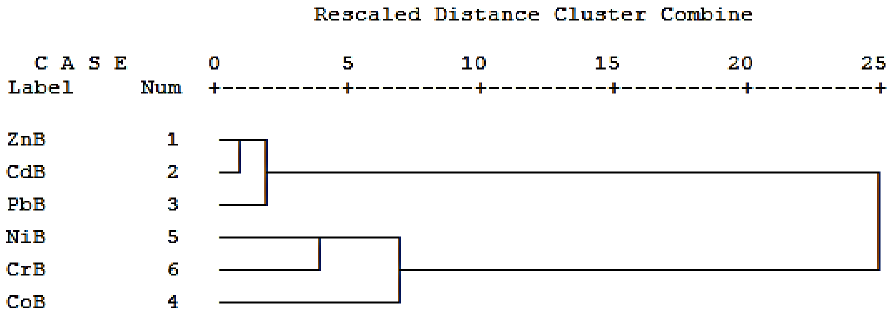


Figure 3. Dendrogram derived from the HCA of heavy metals content in analyzed soils at depth A.

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4. CONCLUSIONS

Results suggested that Co, Ni, and Cr originated from natural sources, while Zn Cd and Pb were mainly affected by anthropogenic sources. Mineralization of the parent rock of Lavrion peninsula consisted of ZnS and PbS, thus the intensive mining and smelting from ancient years up to recent past resulted in high levels of Zn Cd and Pb, which were detected in the entire area, with almost all the samples to exceed the maximum tolerable concentrations. The presence of ophiolites and mafic parts of the parent rock's shales are probably responsible for high Ni concentrations observed in several soil samples. Cr and Co are considered to have also lithogenic origin, although their mobility is limited. Cd is considered to be a serious environmental risk, while for Zn is medium risk, for Ni, Cr and Pb the risk is mostly low and there is no risk at all for Co.

References

[1] Aleksander-Kwaterczak U, Helios-Rybicka E., 2008. Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of South Poland. *J Soils Sediments* **9**:13–22

[2] Chopin, EIB, Alloway BJ., 2007. Trace element partitioning and soil particle characterization around mining and smelting areas at Tharsis, Ríotinto and Huelva, SW Spain. *Sci Total Environ*; **373** (2–3):488–500.

[3] Bhattacharya, A., Routh, J., Jacks, G., Bhattacharya, P., Mörth, M., 2006. Environmental assessment of abandoned mine tailings in Adak, Västerbotten district (northern Sweden). *Appl. Geochem.* **21**, 1760–1780.

[4] Cohen, D., Shen, X., Dunlop, A., Rutherford, N., 1998. A comparison of selective extraction soil geochemistry and biogeochemistry in the Cobar area, New South Wales. *Journal of Geochemical Exploration* **61**, 173–189.

[5] Hirner, A., 1992. Trace element speciation in soils and sediments using sequential chemical extraction methods. *International Journal of Environmental Analytical Chemistry* **46**, 77–85.

[6] Li, X., Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Applied Geochemistry* **16**, 1693–1706.

[7] Pueyo, M., Mateu, J., Rigol, A., Vidal, M., López-Sánchez, J.F., Rauret, G., 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environmental Pollution* **152**, 330–341.

[8] Allison, L.E and Moodie, C.D., 1965. *Carbonate in: Black C.A. Methods of soil analysis*, Part 2. ASA, USA.

[9] Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, Ph., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monitor.* **1**, 57–61.

[10] Li, X.P., Feng, L.N., 2012. Multivariate and geostatistical analyzes of metals in urban soil of Weinan industrial areas, Northwest of China. *Atmospheric Environment* **47**, 58–65.

[11] Lu, A.X., Wang, J.H., Qin, X.Y., Wang, K.Y., Han, P., Zhang, S.Z., 2012. Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China. *Science of the Total Environment* **425**, 66–74.

[12] Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* **65**, 863–872.

[13] Sposito, G., 1989. The Chemistry of Soils. Oxford University Press, New York. 277 pp.

[14] Anju, M., Banerjee, D.K., 2011. Multivariate statistical analysis of heavy metals in soils of a Pb–Zn mining area, India. *Environ. Monit. Assess*. **184**, 4191–4206.

[15] Forghani, G., Mokhtari, A.R., Kazemi, G.A., Fard, M.D., 2015. Total concentration, speciation and mobility of potentially toxic elements in soils around a mining area in central Iran. *Chemie der Erde* **75**, pp. 323–334.

[16] Dimitriadis, A., Vergou, A., Tsompos, P., Stefouli, M., 2002. The use of the results of pollution Lavreotiki peninsula in land use planning. *Proceedings of I 'Scientific Meeting of SE Attica, Studies Southeast Attica*.

[17] Chen, T.B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K., Yu, K., Wu,X., Tian, Q.Z., 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere* **60**, 542–551

[18] Burns, R.G., 1976. The uptake of cobalt into ferromanganese nodules, soils, and synthetic manganese (IV) oxides. *Geochim. Cosmochim. Acta* **40**, 95–102.

[19] Trolard, F., Bourrie, G., Jeanroy, E., Herbillon, A.J., Martin, H., 1995. Trace metals in natural iron oxides from laterites: a study using selective kinetic extraction. *Geochim. Cosmochim. Acta* **59**, 1285–1297.

[20] Adriano, D.C., 2001. *Trace elements in terrestrial environments – Biochemistry, Bioavailability and risks of metals*. Springer – Verlag, New York. pp. 867.

[21] Korfali, S.I., Davies, B.E., 2004. Speciation of metals in sediment and water in a river under lain by limestone: role of carbonate species for purification capacity of rivers. *Adv. Environ. Res*. **8**, 599–612.

ISBN: 978-960-6865-94-7

[22] Akkajit, P. and Tongcumpou, C., 2010. Fractionation of metals in cadmium contaminated soil: Relation and effect on bioavailable cadmium. Geoderma **156**(3-4):126-132.
[23] Favas, P.J.C., Pratas, J., Gomez, M.E.P., Cala, V., 2011. Selective chemical extraction ofheavy metals in tailings and soils contaminated by mining activity. *J. Geochem.Explor*. **111**, 160–171.
[24] Alloway, B. J., 1990. *Heavy metals in soils* p. 100. London: Blackie.
[25] Nannoni, F., Protano, G., Riccobono, F., 2011. Fractionation and geochemical mobilityof heavy elements in soils of a mining area in northern Kosovo. *Geoderma* **161**,63–73.
[26] Martinez-Martinez, S., Acosta, J.A., Faz Cano, A., Carmona, D.M., Zornoza, R., Cerda, C.,2013. Assessment of the lead and zinc contents in natural soils and tailing pondsfrom the Cartagena-La Union mining district, SE Spain. *J. Geochem. Explor*. **124**,166–175.
[27] Anju, M., Banerjee, D.K., 2010. Comparison of two sequential extraction proceduresfor heavy metal partitioning in mine tailings. *Chemosphere* **78**, 1393–1402.
[28] Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. *Journal of Environmental Management* **90**, pp. 1106–1116.

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Migration of Cu, Mn, Fe and Zn at high soil depths due to the disposal of Olive Mill Waste

M. K. Doula[1*], K. Komnitsas[2], A. Zorpas[3], V. Kavvadias[4], D. Zaharaki[2]

[1] Benaki Phytopathological Institute, 8 Stef. Delta str. 14561, Kifissia, Greece
[2] Technical University of Crete, School of Mineral Resources Engineering, 73100 Chania, Crete, Greece.
[3] Department Cyprus Open University, Faculty of Pure and Applied Sciences, Environmental Conservation and Management, Lab of Chemical Engineering and Engineering Sustainability P.O.Box 12794, 2252, Latsia, Nicosia, Cyprus.
[4] Department of Soil Science of Athens, ELGO DEMETER, 1 Sof. Venizelou str. 14123, Likovrisi, Greece.
*Corresponding author: Email: mdoula@otenet.gr

Abstract

Many research works and studies have been carried out so far worldwide to investigate the effect of Olive Mill Wastes (OMW) disposal on soil, focusing mainly on the upper soil horizons (0-30 or/and 0-60cm). The risk of substrate enrichment due to downward migration of constituents present in OMW has been rarely studied, although it poses a significant threat for soil, substrate and groundwater. In the framework of LIFE project PROSODOL LIFE07 ENV/GR/280 “Strategies to improve and protect soil quality from the disposal of olive mill wastes in the Mediterranean region” which was implemented between 2009 and 2012 in Crete, Greece, ten drillholes up to 45 m depth were drilled at a pilot area in Crete, Greece, where three OMW disposal areas were located (two active and one inactive). It was revealed that the risk for ground soil degradation/contamination as well as for contaminant transport due to uncontrolled disposal of OMW is high, especially when soils are poor in clay and the substrate characteristics (e.g. soft fragmented limestone) favour downward migration. Although the obtained results are more pertinent for the disposal areas studied in the frame of PROSODOL, yet, they are indicative and descriptive of the degradation/ contamination risk that may be caused due to OMW disposal in other similar areas. As regards the four metals, Cu, Mn, Fe and Zn, it was observed that if the substrate favours downward migration, then Fe and Zn are very likely to be found in elevated concentrations in higher depths. On the contrary, Cu and Mn were found in low concentrations in all drilling sites.

Keywords: olive mill waste; metals, soil migration; waste management

1. INTRODUCTION

Olive oil industry grows constantly in specific parts of the world. About 750 million olive trees are cultivated and approximately 2.95 million tons of olive oil is produced annually. Most olive oil (98%) is produced in the Mediterranean region, mainly between October and February. Olive oil production results in an annual generation of more than 30 million m^3 of Olive Mill Wastes (OMW). For Mediterranean countries disposal of OMW, mainly if derived from 3-phase centrifugal systems, is considered a major environmental problem [1].

In 2009 the European Commission funded a 4-year demonstration LIFE project, entitled “Strategies to improve and protect soil quality from the disposal of olive mill wastes in the Mediterranean region” (PROSODOL), LIFE07 ENV/GR/000280, which was awarded “Best” LIFE project status in 2014. The project aimed to develop strategies for the protection of Mediterranean soils and water bodies from the disposal of OMW, demonstrate soil remediation methodologies as

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well as develop and propose a legislative framework that could be adopted by the European Union (EU) Member States' national frameworks.

The experience gained through PROSODOL indicates that uncontrolled disposal of OMW increases substantially the risk of soil degradation [2]. For a period of two years several OMW disposal areas in Greece were monitored and the results were assessed in order to identify the effects on soil quality. It was revealed that almost all soil physical and chemical parameters are affected, some of them permanently. Moreover, and in order to assess the potential of deeper soil degradation, ten drillholes were drilled in Crete, Greece. The samples collected were analyzed for a series of parameters. In this study the potential of downward migration of four metals, namely Cu, Mn, Fe and Zn, in higher depths at OMW disposal areas is assessed and discussed. The novelty of this study is high, since so far only very limited publications are available on this issue in international literature [3].

2. MATERIALS AND METHODS

2.1 Area under study

The area under study belongs to the municipality of Rethymnon, Crete, Greece. Ten drillholes were drills near OMW disposal ponds in down-slope points (Map 1) in 2011; at an area of an old, inactive pond, which was covered with soil by the owner; at an area where only sludge from evaporation ponds is disposed; at an area near a river affected by the downward migration of OMW from an active disposal area; and at a control/unaffected area. Table 1 presents the coordinates of the drillholes as well as other useful information.



Map 1. Overall view of the drilling sites (red marks).

2.2. Samples collection and analyses

Samples were collected at different depth intervals varying between 0.5-1.5 m. The samples were analyzed for a series of parameters [4], namely pH, electrical conductivity, organic matter, polyphenols, total Kjeldahl N, NH_4^+, NO_3^-, exch. Mg, PO_4^{3-}, exch. K, exch. Ca, exch. Na, SO_4^{2-}, Cl, B, Cu, Fe, Zn, Mn, Pb, Cr, Ni and Pb. Fe, Cu, Zn and Mn were extracted from soil samples with the

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DTPA method (ISO 14870:2001), which allows the quantification of the available forms of metals. The determination of the metals in the extracts was performed using a VARIAN SPECTRAA 220 Atomic Absorption Spectrometer according to the ISO 11047:1998 method.

3. RESULTS AND DISCUSSION

As it was deduced from the pilot activities and analyses carried out in the frame of PRSODOL project among the four metals, Fe and Cu are more likely to cause phytotoxic effects and long-term soil degradation at OMW disposal areas (measurements conducted at the upper 60 cm soil layer). In specific, the content of available Fe in pond soils and in the direct disposal sites reached very high levels, up to 360 mg/kg, across the soil profile suggesting potential risk for Fe contamination. Even at the inactive pond NF5, it seems that the long period of cease of OMW disposal, which exceeded 10 years, was not sufficient to reduce the available Fe concentration in soils to normal levels. The results of this study confirm the fact that elevated content of polyphenols and other contaminants deteriorate soil properties and affect soil functions and are in agreement with results obtained in other recent studies [5-8].

Table 1. Details of drillholes drilled at the pilot area (referred to Map 1; A, B, and C points are located at the same disposal area, NF4. Similarly, points F, G H points are located at the same area, NF1).

Drilling site, details	Latitude	Longitude	Depth (m)
A: NF4.7. Site between two ponds, accepts often surface OMW disposal	35^{o}18′34.37″N	24^{o}22′05.07″E	4.5
B: NF4.8. Site between two ponds, accepts often surface OMW disposal	35^{o}18′34.51″N	24^{o}22′06.63″E	9.0
C: NF4.20. Site that is affected by two ponds, accepts often surface OMW disposal	35^{o}18′34.44″N	24^{o}22′07.50″E	45.0
D: NF5. Site that is affected by the disposal of OMW from two ponds (slope 15%)	35^{o}18′34.02″N	24^{o}22′10.25″E	6.0
E: RIVER. Site near a river in the pilot area. Potential pollution by two ponds	35^{o}18′32.44.″N	24^{o}22′18.17″E	40.0
F: NF1 Pond. Drillhole at 1m distance from the walls of a disposal pond	35^{o}12′22.02″N	24^{o}32′6.98″E	42.0
G: NF1.1. Site 5m away from a disposal pond that is indirectly affected by OMW	35^{o}19′16.84″N	24^{o}24′45.24″E	51.5
H: NF1 Sludge disposal. Site at which only sludge from a pond is disposed periodically	35^{o}19′16.84″N	24^{o}24′45.24″E	45.0
Inactive Pond: Site at an inactive (for 4 years) evaporation pond. The pond has been covered with soil the last 4 years	35^{o}20′41.30″N	24^{o}25′50.70″E	24.0
Control: Site not affected by the disposal of OMW.	35^{o}18′16.10″N	24^{o}22′06.93″E	5.0

Results on available Cu indicated that potential toxic Cu concentrations can be found in both active (up to 21 mg/kg) and inactive (up to 18 mg/kg) pond soils, however very high Cu levels were only detected in a small percentage of the entire Cu dataset (5%). Long-term disposal of OMW in

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evaporation ponds increases also the availability of Zn to high levels (up to 31mg/kg) in surface soil (0- 50cm), which are not considered toxic though. Regarding available Mn, there were cases in which increased Mn concentrations were measured. However, in some sites the high natural Mn content in soil was decreased after OMW disposal, mainly due to waste's acidity, which resulted in Mn solubilization from the soil fraction and parent rocks [9-10].

Figures 1-4 present the concentrations of Fe, Cu, Zn and Mn in the samples collected from all drilling sites.

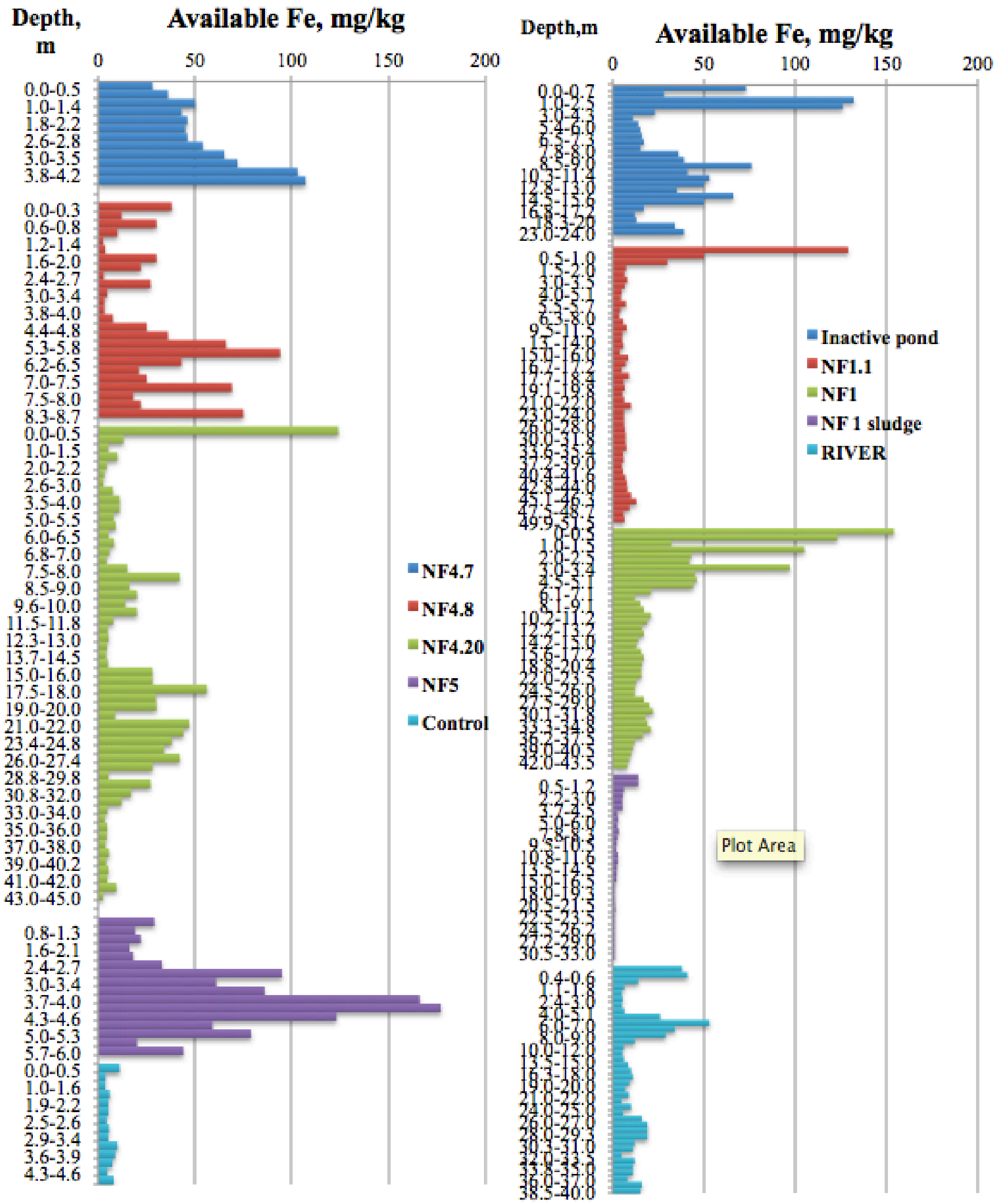


Figure 1. DTPA-extractable Fe in the samples collected from the ten drillholes drilled in the pilot area in Crete, Greece.

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3.1 Disposal area NF4 (drillings NF4.7, NF4.8, NF4.20)

These three sites (Map 1 and Table 1) are affected by OMW disposal (a) directly, by surface disposal, and (b) indirectly, by subsurface OMW migration. From the four metals studied, Fe and Zn concentration was high (up to 100mg/kg and to 2mg/kg respectively). On the other hand, Cu is not considered as potential threat, although its concentrations in most samples were somehow higher compared to control samples. Nevertheless, leached Cu concentrations are very low and similar to Mn. Therefore, although the substrate’s properties (soft fragmented limestone) in the study area allows downward migration of OMW, not all elements are likely to be found in high concentrations in high depths. This is also true for the four metals investigated in this study.

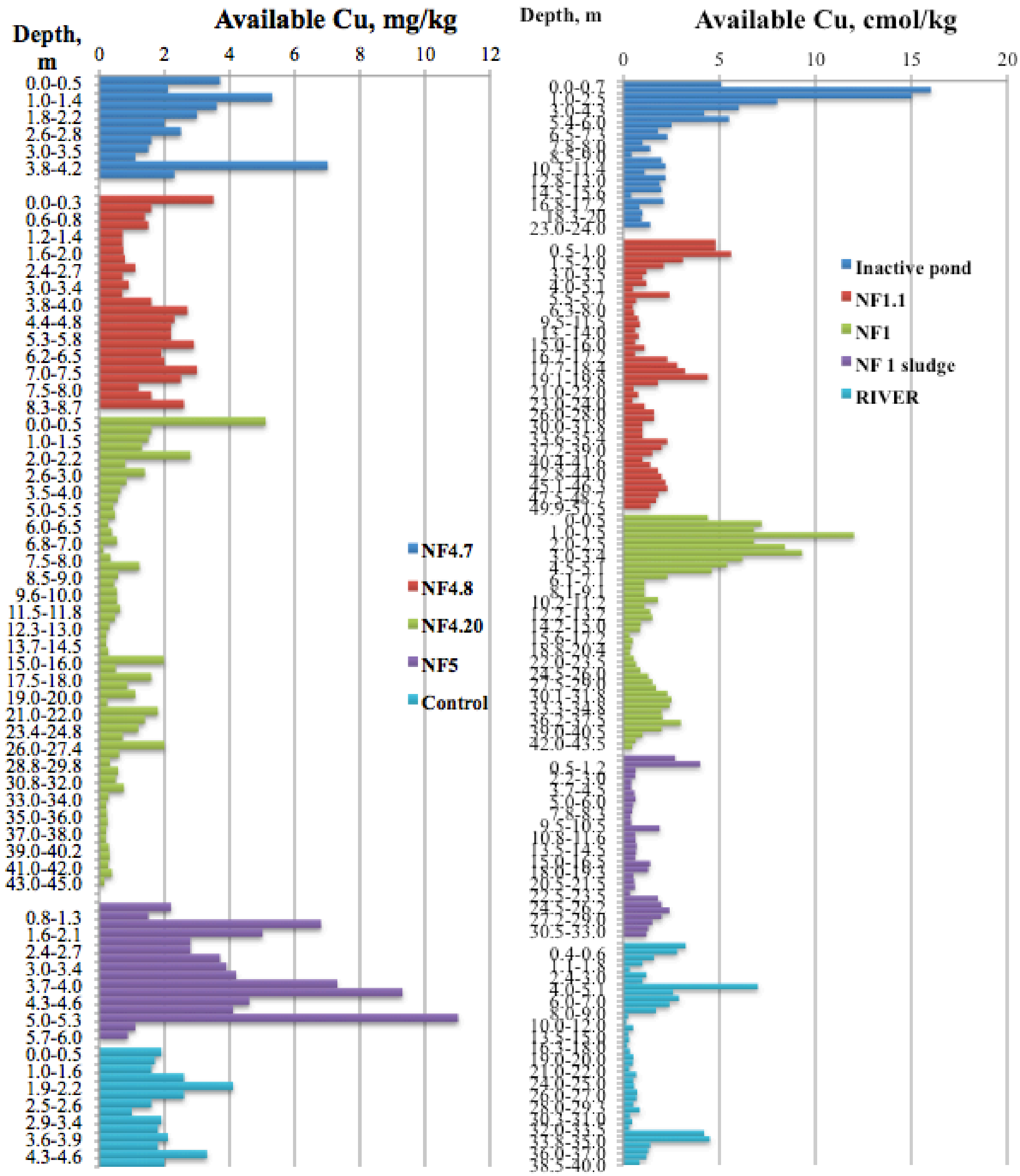


Figure 2. DTPA-extractable Cu in the samples collected from the ten drillholes drilled in the pilot area in Crete, Greece

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3.2. Disposal area NF5 (inactive site)

The soils of the area NF5, which was used for OMW disposal for more than 10 years, are characterized by high sand content varying between 50% and 90%. In this area, disposal of OMW was ceased 5 years before drillholes were drilled, while the owner filled the old pond with soil transferred from another nearby area. The old pond was almost 3m deep, so the analyses results for the first 3m of soil were not considered in this study. In this case, due to the high sand content and thus the high permeability of the upper soil layers, OMW migration to higher depths was easier, as it was confirmed also from the high concentrations of all four studied metals, compared to the control samples. Another significant aspect, which can be also seen in Figures 1-4, is that the increasing/decreasing trend in metals' concentrations is the same for all of them at the same depths.

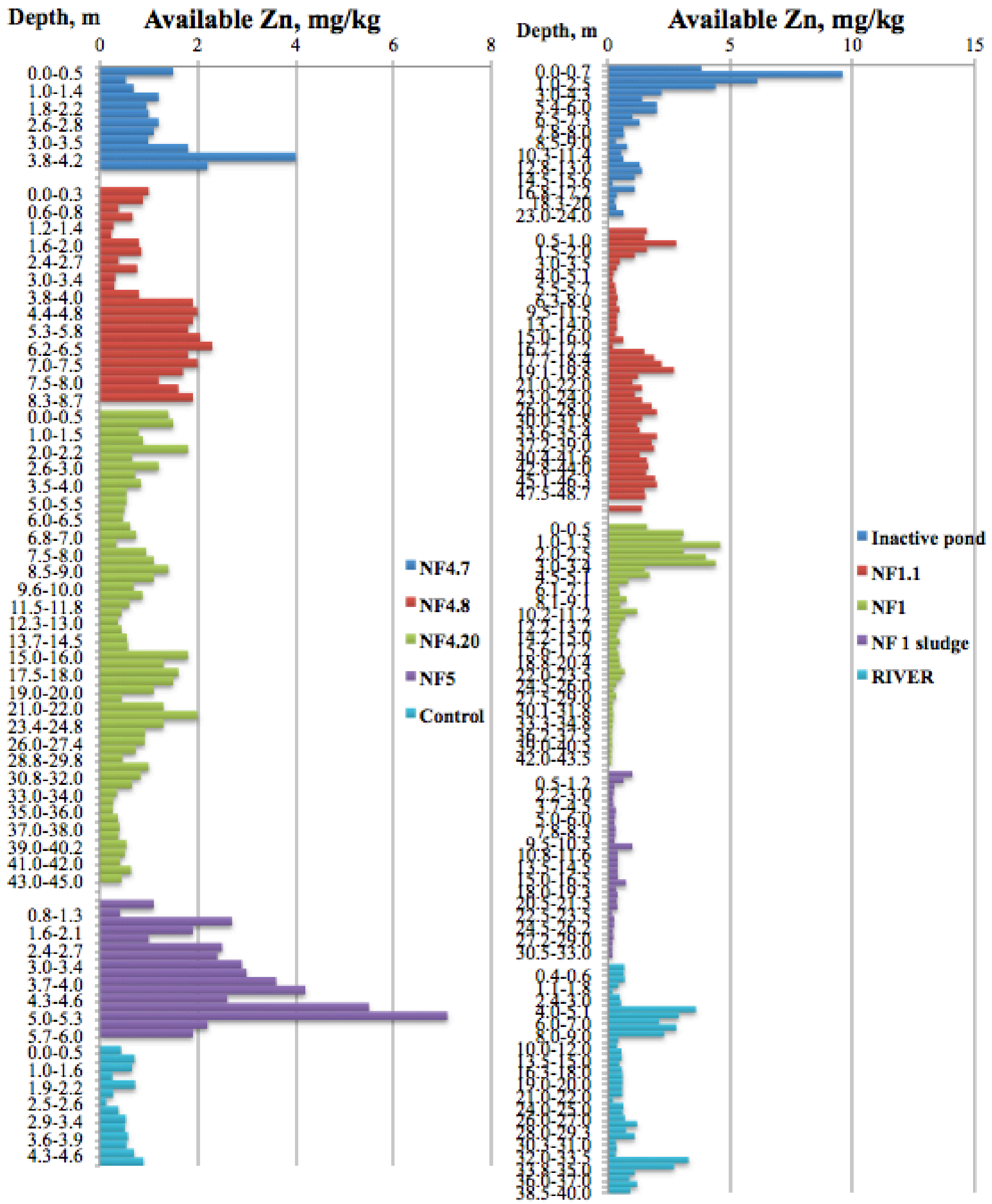


Figure 3. DTPA-extractable Zn in the samples collected from the ten drillholes drilled in the pilot area in Crete, Greece

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3.3. River Site

The drilling site "E-River site" was located 100m downhill the NF4 OMW disposal area. A drillhole was drilled there in order to investigate the possibility of OMW migration through the subsurface. It can be seen in Figures 1-4, that Fe and Zn are the two metals with the higher concentration, mainly at soil depths up to 9.0 m. However, even though the substrate at NF4 allows underground OMW migration, the measured metals concentrations are maybe due to the presence of other contaminants, since sewage from neighboring villages is discharged into river water.

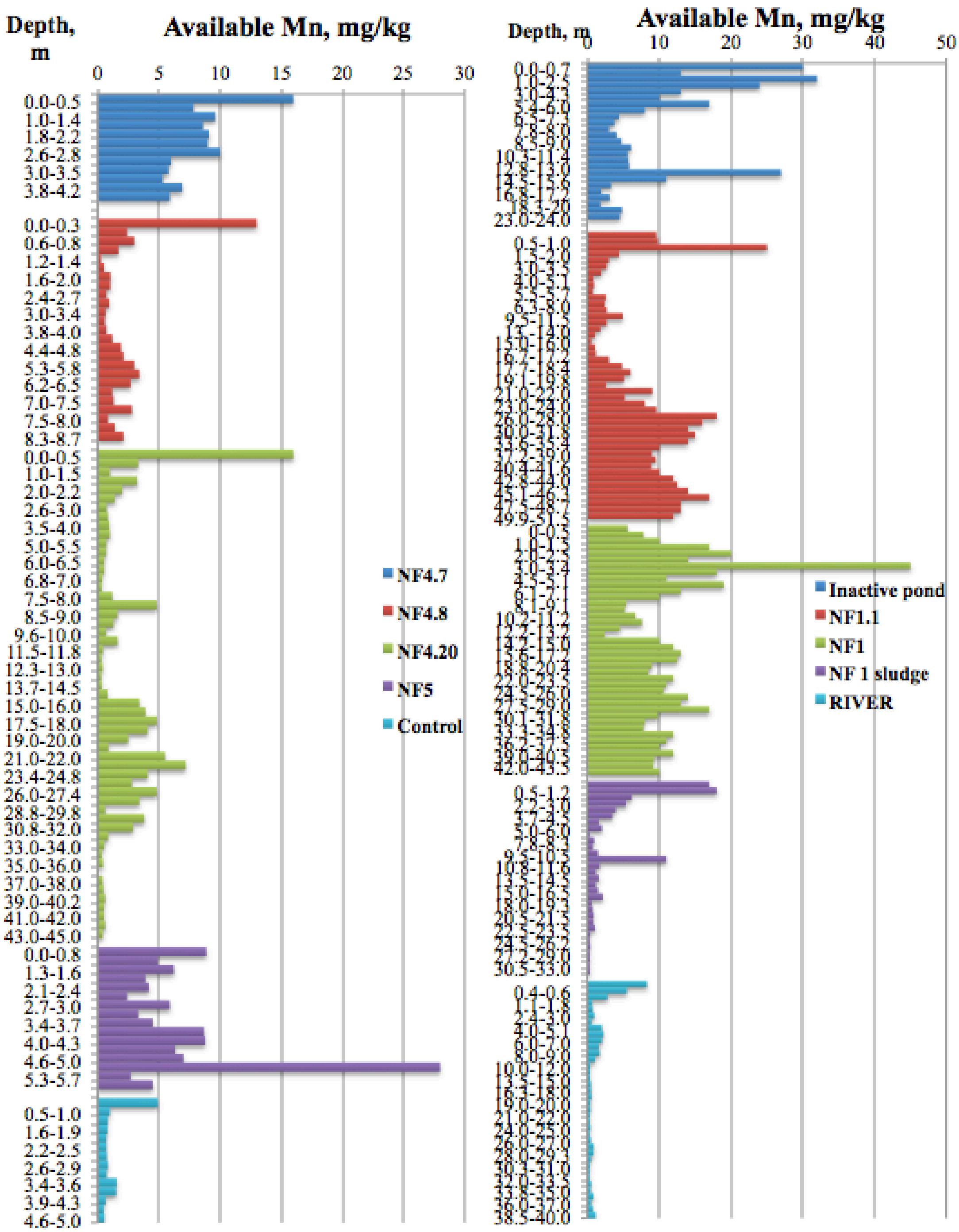


Figure 4. DTPA-extractable Mn in the samples collected from the ten drillholes drilled in the pilot area in Crete, Greece.

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3.4. Disposal area NF1 (NF1, NF1.1, NF1-sludge)

The three sites selected in this disposal field are located in the same direction. In specific, NF1-sludge is a site where OMW sludge was periodically disposed for several years. NF1 is a site very near to the disposal pond of the area, while NF1.1 is located 4 meters away from NF1 (the slope of the area is almost 4-5%). The soil in the area is similar to the soil at NF4, i.e. rich in clay, $CaCO_3$ and has slightly alkaline pH (7.5-7.9). However, the substrate of NF4 consists mainly of soft fragmented limestone while in NF1 the limestone is not fragmented. This difference prevented OMW migration and protected soils in higher depths.

As for all other soil parameters [2] it was observed that the higher concentrations of the four metals were recorded at low depths (up to 4-5 m). Available Mn was the only exception but this is mainly due to the high background value of this element in the area under study. Regarding Mn, it has to be mentioned that it is an element which is characterized by high mobility over a very broad pH range. Also, Mn^{2+} is characterized by low reduction potential, thus its tendency for reduction is rather limited. The way Mn will behave in soil solutions and pore water depends also on the organic matter content of soils as well as the prevalence of oxic or anoxic conditions [11,12].

4. CONCLUSIONS

The risk for ground soil degradation/contamination as well as for contaminants migration due to uncontrolled disposal of OMW is considered high especially in soils poor in clay and when the substrate characteristics, e.g. presence of soft fragmented limestone, favour downward migration of OMW. Although the obtained results are specific for the disposal areas investigated in the frame of PROSODOL project, yet, they are indicative and descriptive of the degradation risk that may be caused due to OMW disposal in other similar areas. Analyses of soil samples from ten drillholes drilled in three OMW disposal sites in Crete, Greece, exhibiting different characteristics provided similar results, i.e. OMW migration through the substrate is possible and mainly depends on substrate properties. This study focuses on the determination of the concentrations of available forms of Fe, Cu, Zn and Mn at high depth. It is deduced that among the OMW constituents that can be found at high concentration even at 45m depth, Fe is also included. If the substrate favours downward OMW migration, then Zn is very likely to be traced also at higher depths. On the contrary, available forms of Cu and Mn were traced in low concentrations in all areas under study.

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References

[1] Niaounakis, M., Halvadakis C.P. 2006. *Olive processing waste management - Literature Review and Patent Survey*. 2nd ed. Elsevier Ltd, p 30.
[2] LIFE Prosodol, 2012. Strategies to improve and protect soil quality from the disposal of Olive Oil Mill Wastes in the Mediterranean region, http://www.prosodol.gr/?q=node/3445 (assessed April 1, 2016).
[3] Mahmoud, M., Janssen, M., Haboub, N., Nassour, A., Lennartz, B. 2010. The impact of olive mill wastewater application on flow and transport properties in soils, *Soil Tillage and Research*, **107(1)**, 36-41.
[4] Page, A.L., Miller, R.H., Keeney, D.R. 1982. *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*. American Society of Agronomy, Madison, Wisconsin.

ISBN: 978-960-6865-94-7

[5] Piotrowska, A., Iamarino, G., Rao, M.A., Gianfreda, L. 2006. Short-term effects of olive mill waste water (OMW) on chemical and biochemical properties of a semiarid Mediterranean soil, *Soil Biology and Biochemistry*, **38(3)**, 600-610.
[6] Barbera, A.C., Maucieri, C., Cavallaro, V., Ioppolo, A., Spagna, D. 2013. Effects of spreading olive mill wastewater on soil properties and crops, a review. *Agricultural Water Manag*ement, **119**, 43-53.
[7] Belaqziz, M., El-Abbassi, A., Lakhal, E.K., Agrafioti, E., Galanakis, C.M. 2016. Agronomic application of olive mill wastewater: Effects on maize production and soil properties. *Journal of Environmental Management*, **171**, 158-165.
[8] Komnitsas, K., Modis, K., Doula, M., Kavvadias, V., Sideri, D., Zaharaki, D. 2016. Geostatistical estimation of risk for soil and water in the vicinity of olive mill wastewater disposal sites. *Desalination and Water Treatment,* **57(7)**, 2982-95.
[9] Kavvadias, V., Doula, M.K., Komnitsas, K., Liakopoulou N. 2010. Disposal of olive oil mill wastes in evaporation ponds: Effects on soil properties. *Journal of Hazardous Materials*, **182**, 144-1554.
[10] Kavvadias, V. Komnitsas, K., Doula, M.K. 2011. *Long term effects of Olive Mill Wastes disposal on soil fertility and productivity*. In: Hazardous Materials-Types, Risks and Control, S.K. Brar (ed.) Nova Science Publishers, Inc., ISBN 978-1-61324-425-8.
[11] Groudev, S.N., Spasova, I.I., Georgiev, P.S., Komnitsas, K. 2001. Bioremediation of soil contaminated with radioactive elements. *Hydrometallurgy*, **59**, 311-318
[12] Komnitsas, K., Bazdanis, G., Sahinkaya, E., Bartzas, G., Zaharaki, D. 2013. Removal of heavy metals from leachates using permeable reactive barriers filled with reactive organic/inorganic mixtures. *Desalination and Water Treatment,* 51, 3052-3059.

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Environmental Informatics

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

An automated, GIS based decision support system for fertilizer use in the basin of river Aggitis, Northern Greece

I. Iordanidis[1], N. Kamidis[2], S. Orfanidis[2], P. Anagnostopoulos[1*], E. Malkakis[3], A. Antoniadis[4]

[1] Department of Civil Engineering, Aristotle University Thessaloniki, Greece
[2] ELGO-DEMETER, Fisheries Research Institute, NeaPeramos-Kavala, Greece
[3] Department of Environment and Hydroeconomy, Regional Unit of Drama, Region of East Macedonia and Thrace, Greece
[4] IT Department, Regional Unit of Drama, Region of East Macedonia and Thrace, Greece
* Corresponding author: Email: anagnost@civil.auth.gr

Abstract

The extensive use of fertilizers constitutes a significant source of pollution for water bodies, especially when the quantity used exceeds the limits specified by directives. The online application, which is presented in this paper, aims to inform farmers and authorities for the impact of fertilizer and pesticide use in the basin of river Aggitis. The core of the application is the AGNPS model, which provides daily estimations of fertilizer runoff to the water bodies. AGNPS output is processed by GIS in order to create interactive guideline maps, which are uploaded to a webpage. The guidelines refer to the use of fertilizers and pesticides, by providing farmers with a YES/NO instruction, depending on a five-day forecast of fertilizer runoff. The output of AGNPS is also processed in order to provide local authorities with detailed five-day forecast of rainfall spatial distribution, and an estimation of the quantity of fertilizers that could potentially end up into the region's streams. The application is expected to increase the awareness of farmers regarding the environmental impact of their activities and to assist them in the better management of their resources.

Keywords: DSS; GIS; AGNPS; nitrate pollution; fertilizers

1. INTRODUCTION

In various situations, the complexity of a scientific application poses difficulties on the exploitation of its output by potential users, especially if interaction is required from their side. The application presented here aims to provide end users, both famers and officials of local authorities, with comprehensive instructions for the use of fertilizers and pesticides. The instructions are based on the results of simulations of the AGNPS model, which are performed on a daily basis and then are processed using ArcGIS Python Scripting and Spatial Analysis. The final instructions, which are derived from the results, are provided online in a YES/NO format, while the website supports the use of location services of cellular phones, in order to facilitate its use by farmers, who would prefer a simple instruction that would refer locally to their own landplot.

The use of GIS in the decision making process is widespread in a variety of application fields. They are used in decision support for land suitability studies [1, 2], crop planning [3], pesticide leaching [4], nitrate fertilizer use [5] etc. Although Decision Support Systems (DSS) are in use for more than twenty years [6, 7], in the majority of occasions the application interface required inputs from the end user’s side, which rendered necessary a minimum level of expertise in the use of such systems. Therefore, in many cases, the group that was aimed to benefit from the development of such an application, farmers in the present case, did not take advantage of its benefits, due to poor acquaintance with computer use.

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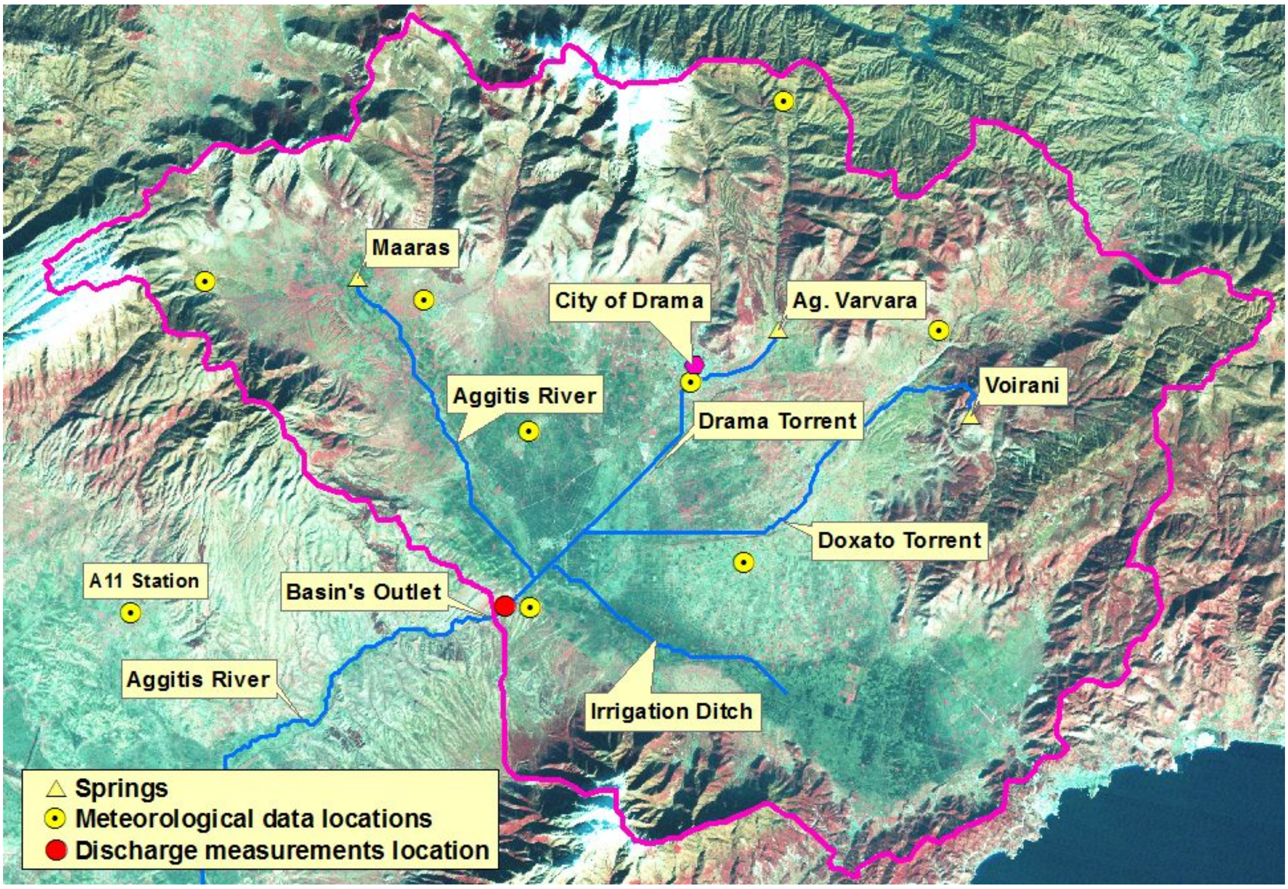


Figure 1. The study basin with its hydrographic network and the meteorological data locations.

In order to address this issue, the application which is presented in this paper, provides information and guidelines without requiring any action from the user's side. All required inputs are either built in the model's parameters or are automatically generated with the use of computer scripts. This process required careful planning and design at the stage of the creation of the application, in order to identify the parameters that would require daily input updates and those that would be used as constant variables for the period that the application will be used. The study area, for which this system is applied and used for the first time in Greece, is located in the basin of river Aggitis, in Eastern Macedonia, Greece, as illustrated in Figure 1. The source of the maps used in the paper is the web page of the Drama Prefecture (www.pedramas.eu). The application can be accessed via the same web page of the Drama Prefecture.

2. MATERIALS AND METHODS

2.1 Description of AGNPS

The core of the application presented in this paper is the AGNPS model. AGNPS is a daily time-step, distributed model, which enables the modeling of the various processes and parameters that affect nitrate pollution, allowing the creation of a detailed model of the study area [8]. The required inputs include ground elevation, soil texture, land use, data on cultivation and irrigation practices, fertilizer use and crop requirements. The model also requires extensive rainfall and climate data (wind speed, relative humidity, temperature and solar radiation).

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AGNPS was employed in order to provide daily estimations of the basin's response to the use of fertilizers and pesticides and uses these results in order to issue daily guidelines for farmers and public services. The primary aim of the application is to deter farmers from applying fertilizers or pesticides on their fields, when there is high probability that they will be transferred to the basin's recipient stream, thus resulting in a waste of their resources, both economic and material, and in ecological pressure on the environment.

AGNPS was calibrated using data for 2008 and validated with data for 2009 [9]. The meteorological data series used for the calibration process were taken from the records of the station A11 close to the basin (Figure 1), assuming that conditions were not substantially different inside the basin. Although meteorological gauges were in operation within the study area [10], their data were available on a monthly basis, therefore they were unsuitable for use by AGNPS, which requires data on a daily basis. The objective of the calibration and validation process was to obtain values of spring discharge and nutrient runoff as close as possible to the measured ones. This was achieved by changing the values of fertilizer application rate and spring discharge, while maintaining all variable values, which were related to crop cultivation, constant, according to data available for the whole region. The quantities that were calculated refer to annual totals. Records for the nutrient loads were available at the basin's outlet (Figure 1) for years 2008 and 2009, whereas for the river discharge only for the year 2009. After careful examination of the climate conditions for the years 2008 and 2009, it was concluded that the conditions did not vary significantly; therefore it was assumed that the river discharge was the same for both years. This assumption was necessary in order to calibrate the runoff component of AGNPS for the year 2008.

The model was verified for the year 2009, by using the parameter values that were calibrated for the year 2008. The deviation of runoff was calculated at 1.2% and the deviation of nutrient load at 14%. These deviations are well within the model's performance limits, according to previous studies [11].

Table 1. Calibration and validation results for AGNPS

CALIBRATION RESULTS			
Simulation Parameter	**2008 Recorded Data**	**2008 Simulated Data**	**Deviation**
Water volume at the basin's outlet (m^3)	433,895 x 10^6	452,790 x 10^6	4.3%
Nutrient load at the basins outlet (tn)	244.28	240.55	-1.5%
VERIFICATION RESULTS			
Simulation Parameter	**2009 Recorded Data**	**2009 Simulated Data**	**Deviation**
Water volume at the basin's outlet (m^3)	433,895 x 10^6	428,635 x 10^6	-1.2%
Nutrient load at the basins outlet (tn)	259.83	221.88	-14.6%

After AGNPS was calibrated according to the basin's characteristics, the daily input parameters should be specified. Land use, irrigation, crop and cultivation data were all maintained as constants, according to their calibrated values. The application provides guidelines for the current day and a four-day forecast. Therefore, meteorological data should be a daily input variable. The meteorological data for the simulation period are downloaded automatically using a Python script, which updates the meteorological data file used by AGNPS on a daily basis. These data are obtained from nine locations in the basin, as indicated in Figure 1, and contain five-day values for rainfall, temperature, wind speed and sky cover.

As stated before, the primary objective of the application is to provide guidelines to all farmers in the region on the use of fertilizers and pesticides. In order to achieve this goal and provide useful information to any user, it was decided that the model will operate on the assumption that all users will apply their fertilizers simultaneously at all parts of the region. This assumption, although leads

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to an exaggerated estimation of fertilizer runoff at the basin's outlet, was essential in order to produce results that would inform individual users about the waste of their resources to runoff.

2.2 GIS component

Another significant component of the application is the spatial analysis by GIS. The Spatial Analyst extension of ArcGIS 9.3 was used in order to create the information maps that would provide the necessary guidelines to the end users. The maps are delivered in KML file format, which are uploaded to the application's webpage. Each map consists of colors that correspond to the results of the model for any specific point, according to the desired guideline. The user can see the guideline by clicking on the desired point on the relevant map, as shown in Figure 2.



Figure 2. Guideline sample map for pesticides.

The entire procedure of performing spatial analysis of the data and creating the final maps is completely automated by using the ArcGIS built-in Python scripting feature. All analyses were programmed into the ArcGIS Model builder and exported as Python scripts. An AGNPS result file, which was updated daily, was used as input for the GIS and then the final map was produced. The automated process ensures that no human intervention is required in the procedure of producing the maps, thus allowing the continuous function of the application, regardless of holidays or other probable causes that might hinder an operator from uploading the results on the web site. The GIS model structure used is depicted in Figure 3.

Initially, meteorological data are collected via an automated Python script and the AGNPS inputs are updated. Then, an AGNPS simulation is performed and a result file with estimations of nutrient loads in the basin is produced. The rainfall values for the nine locations and the nutrient loads for the cells, in which the basin is discretized, are used to produce an ArcGIS shapefile which contains extrapolated values for rainfall and nutrient load, for the entire basin's area (1). A new field is added to this shapefile, with the intention to be filled (populated) with the YES/NO guidelines. The YES/NO value is determined according to each cell’s value (either rainfall or nutrient load) and then assigned to each record (2). The cells with the same YES/NO value are dissolved to a single feature (3), in order to create the shapefile which contains the YES/NO guidelines (4). This

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shapefile is converted to an ArcGIS layer, afterwards a specific symbology is applied in order to create a layer with the desired color scheme (5) and then the layer is saved on the server's hard disk (6). The guideline layer (7) is converted to a KML file (8) and uploaded to the application's web site (9). After this process, the added field from step (2) is deleted from the shapefile (10) in order to retain the initial shapefile and use it again the next day.

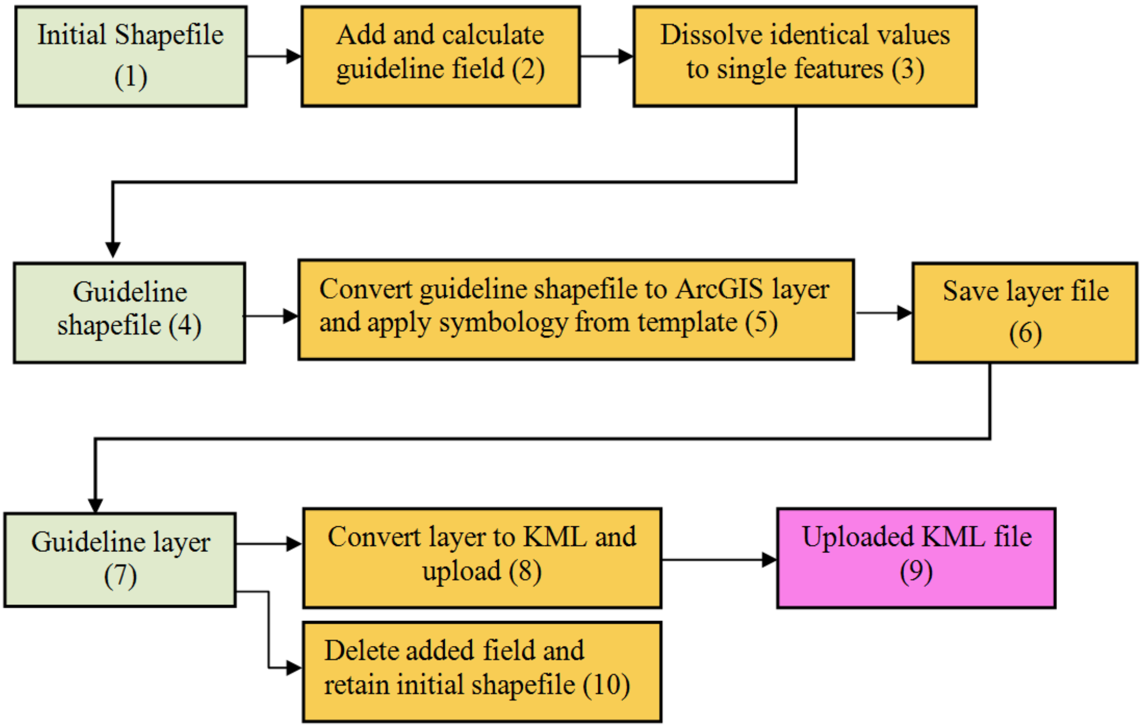


Figure 3. GIS model for the generation of the final guideline map.

2.3. Automated processing and scripting

The entire process of modifying the daily AGNPS inputs, performing AGNPS simulation and the subsequent spatial analysis of the results via GIS, and, finally, uploading the results to the application's webpage, is completely automated. A set of Python computer scripts, scheduled to be executed consecutively via the Windows Task Scheduler, downloads the meteorological data, modifies the AGNPS input data for the simulation period (in order to match the current day and a four day forecast each time) and begins the AGNPS simulation. After the simulation is completed, another script modifies the AGNPS result file in a format that can be used by ArcGIS and launches the Spatial Analysis process. Finally, the maps which are produced are uploaded, by another script, to the server of the application, as explained previously. This process is completed in approximately 45 minutes and is executed on a daily basis.

3. RESULTS AND DISCUSSION

The application is available online and accessible to the public since the beginning of November 2015. Up to date, its predictions have been in accordance to the observations of local authorities. The application produces four distinct types of maps, depicted in Figures 4 to 7. Two of them are aimed to be used by local farmers and provide simple YES/NO instructions according to the results of the AGNPS simulations, and the other two aim to assist local authorities and provide results in

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detail. High fertilizer and pesticides runoff rates produce a “NO”, while low runoff rates produce a “YES”, which informs a farmer that it is safe to use fertilizers on his field. Due to the assumption of uniform fertilizer use in the basin and in order to deter individual farmers from using their resources when there is high risk of waste, the quantity that would produce a “NO” result was set as low as 10 kg per cell (Figure 4). All maps are available as individual links in the application’s web site. Users can select the relevant type of map and then, from the list of five maps (one for each day of the five-day simulation) for the selected type, choose the map which corresponds to the day for which information is required. In case that a computer is not available, the maps can be accessed with a smartphone.

Responding to a request by the farmers' unions, a map similar to the map of fertilizer use is provided regarding the use of pesticides. In this map, the YES/NO instruction is based solely on the anticipated daily rainfall height. Rainfall heights above 2 mm/day produce a “NO” instruction, in order to prevent pesticide leaching (Figure 5).



Figure 4. Guideline map for fertilizer use for famers.



Figure 5. Guideline map for pesticide use for famers.

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Detailed maps containing more information are provided to the local authorities, or to users who require more information. The map which refers to fertilizer runoff provides data on the estimated quantity of fertilizers in each location (Figure 6), while a detailed map for the spatial distribution of rainfall height is also provided (Figure 7). This additional information can be used in order to assist local authorities in the better management of the basin.

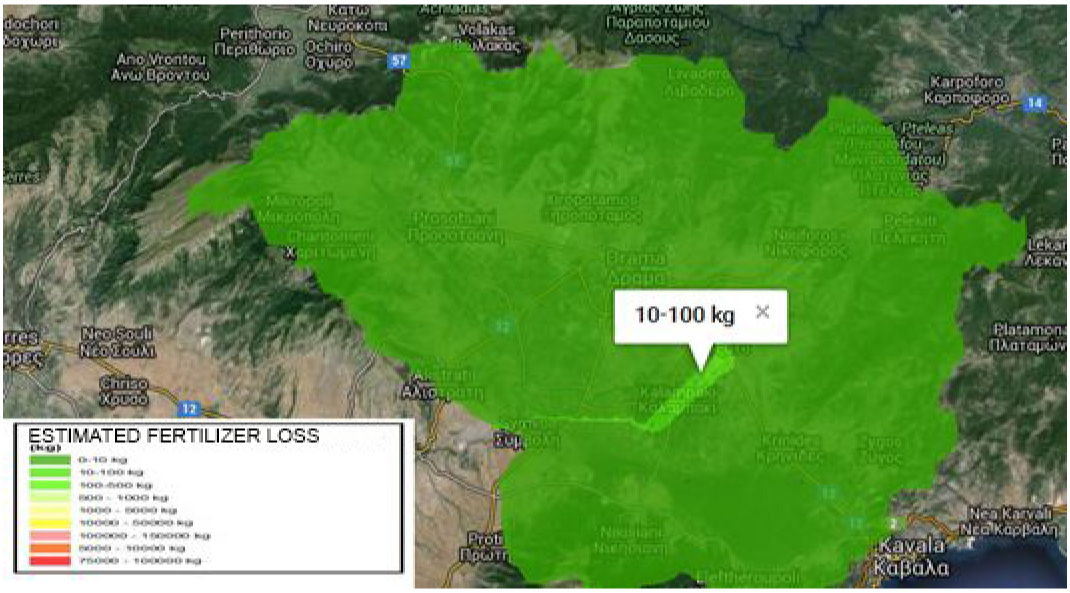


Figure 6. Guideline map for fertilizer runoff for local authorities.

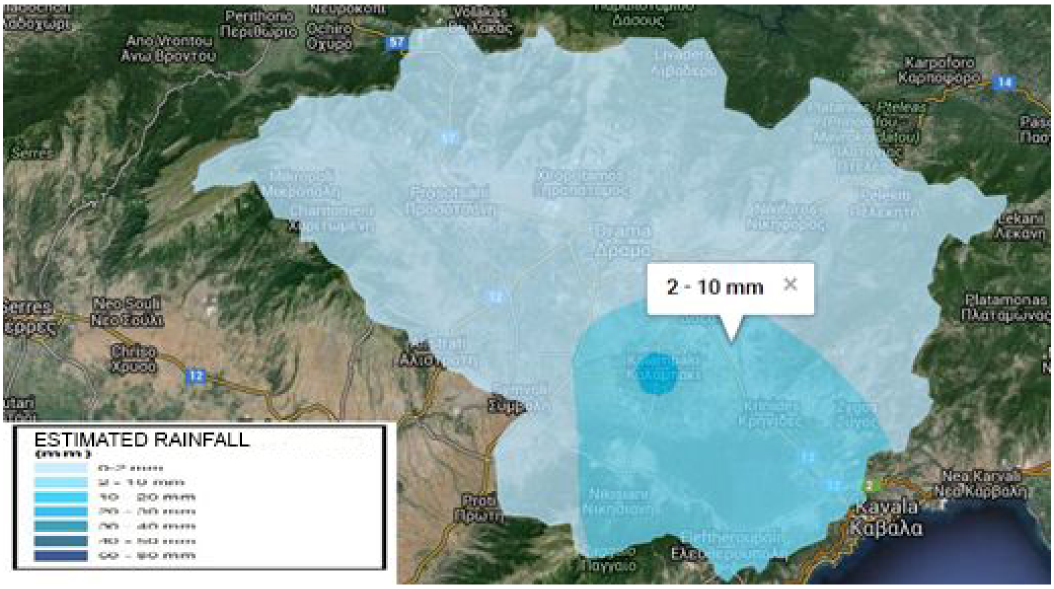


Figure 7. Guideline map for rainfall height for local authorities.

4. CONCLUSIONS

The online application described in this paper, aims to inform farmers and authorities for the impact of fertilizer and pesticide use in the basin of river Aggitis. The core of the application is the AGNPS model, which provides daily estimations of fertilizer runoff to the water bodies. This web application provides a user friendly environment and comprehensive guidelines to users who are not acquainted to the use of computers. Since it does not allow, in its present form, the examination of

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scenarios according to users' intentions, its primary advantage lies in the fact that it does not require any form of interaction with potential users. This makes it more attractive to users who require results and instructions without the need to insert input data. Taking into account that the majority of farmers, who are the main target group of users, belong to that category, the application is expected to be widely used by the local farmer community. Up to date, the observations of officials of local authorities confirm the reliability of the application's forecasts, increasing its credibility among farmers.

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References

[1] Walke, N., Obi Reddy, G.P., Maji, A.K., Thayalan, S., 2012. GIS-based multicriteria overlay analysis in soil-suitability evaluation for cotton (Gossypium spp.): case study in the black soil region of Central India. *Computers & Geosciences,* **41**, 108–118

[2] Ismail, M., Abdel Ghaffar, M.K., Azzam, M.A., 2012. GIS application to identify the potential for certain irrigated agriculture uses on some soils in Western Desert, Egypt. *The Egyptian Journal of Remote Sensing and Space Sciences,* **15**, 39–51.

[3] Rao, M., Fan, G., Thomas, J., Cherian, G., Chudiwale, V., Awawdeh, M., 2010. A web-based GIS Decision Support System for managing and planning USDA's Conservation Reserve Program (CRP). *International Journal of Applied Earth Observation and Geoinformation,* **12**, 190–200.

[4] Ki, S.J., Ray, C., 2015. A GIS-assisted regional screening tool to evaluate the leaching potential of volatile and non-volatile pesticides. *Journal of Hydrology,* **522**, 163–173.

[5] Da-Wei, Z., Yao, H., Jin, Z.G., Zhang, W., Jiang, J., 2008. Nitrogen Management Evaluated by Models Combined with GIS - A Case Study of Jiangsu Croplands, China, in 2000. *Agricultural Sciences in China* **7(8),** 999-1009.

[6] Negahban, B., Fonyo, C., Boggess, W.G., Jones, J.W., Kampbell, K.L., Kiker, G., Flaig, E., Lal, H., 1995. LOADSS: A GIS-based decision support system for regional environmental planning. *Ecological Engineering,* **5**, 391-404.

[7] Lilburne, L., Watt, J., Keith, V., 1998. A prototype DSS to evaluate irrigation management plans. *Computers and Electronics in Agriculture*, **21**, 195–205.

[8] Binger, R. L, Theurer, F. D., 2001. AGNPS98: A suite of water quality models for watershed use. *Proceedings of the 7th Federal Interagency Sedimentation Conference: Sediment monitoring, modelling and Managing,* Reno, NV.

[9] Iordanidis, I., Anagnostopoulos, P., 2012. Investigation of nitrate pollution in the plain of Drama from agricultural activities. *Proceedings of the 10th International Conference on Hydroinformatics*, Hamburg, Germany.

[10] Iordanidis, I., Anagnostopoulos, P., 2012. Control of reliability of a generalized linear model for the generation of stochastic rainfall series. *Hydrotechnica, Journal of the Hellenic Hydrotechnical Association*, **21**, available in web (in Greek).

[11] Licciardelo, F., Zema, F.D., Zimbone, S.M., Binger, R.L., 2007. Runoff and soil erosion evaluation by the AnnAGNPS model in a small Mediterranean watershed. *American Society of Agricultural and Biological Engineers,* **50**, 1585-1593.

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Classification of rainfall data in the region of Serres using fuzzy logic

N. Samarinas, C. Evangelides*, C. Tzimopoulos

Department of Hydraulics and Transportation Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
*Corresponding author: Email: evan@vergina.eng.auth.gr

Abstract

The aim of this paper is the classification of rainfall data using fuzzy logic in order to examine whether there are similarities among rainfall stations. The data was taken from 7 rainfall stations in the region of Serres in Northern Greece and was used to calculate correlation coefficients. Then with the fuzzy logic method the rainfall stations were categorized and classified according to the reliability degree. Due to the complexity of the problem, a software in Matlab environment was created, which accepts the rainfall data, calculates the correlation coefficients, creates graphs and does all the necessary steps to provide the final classification of rainfall stations.

Keywords: fuzzy logic; rainfall data; classification; tolerance-equivalence relations; Matlab

1. INTRODUCTION

In recent years the domain of fuzzy logic has made enormous progress and is taught in many countries around the world at both undergraduate and postgraduate level, while its implementation has found fertile ground in many branches of engineering sciences. The fuzzy logic is derived from the development of fuzzy sets theory of Lofti Zadeh, is well structured and performs well in ambiguous or uncertain environment [1]. Contrary to the Aristotelian logic or the classical logic, which is a binary logic, fuzzy logic is multivalued and variables can take infinite values in truth degree ranging between 0 and 1. When linguistic variables are used, the degree of truth is presented by specialized functions. Consequently, the fuzzy sets work in ambiguous and uncertain environment and give meaningful results for humans; results that are close to the human way of thinking and expression [2].

In accordance with Cox [3], it is commonly accepted that the techniques based on classical logic have proved unsuccessful to approximate the procedures of common sense, learning from experience, etc. Fuzzy logic shines in these fields by focusing on the representation of the ambiguity, imprecision and uncertainty to achieve satisfactory solutions. Zadeh proposed the principle of incompatibility, according to which: ***as the complexity of a system increases, human ability to make precise and relevant (meaningful) statements about its behavior diminishes until a threshold is reached beyond which the precision and the relevance become mutually exclusive characteristics. It is then that fuzzy statements are the only bearers of meaning*** [4].

The aim of this paper is the classification of rainfall data using fuzzy logic in order to examine the degree of similarity among rainfall stations. The complexity of classification of rainfall data requires the construction of customized software in MATLAB.

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2. MATERIALS AND METHODS

2.1 Methodology

All basic and necessary steps for achieving rainfall data classification are as follows:

1) Acquisition of rainfall data,
2) Calculation of correlation coefficients,
3) From the correlation coefficients a matrix $\tilde{R}_1$ is obtained, called tolerance matrix, with the following properties:

- $a_{ij} \in [0,1]$
- $a_{ii} = 1$ *(reflexivity)*
- $a_{ij} = a_{ji}$ *(symmetry)*

4) Matrix $\tilde{R}$ is obtained from $\tilde{R}_1$ which is called equivalence matrix having the three following properties:

- $a_{ii} = 1$ *(reflexivity)*
- $a_{ij} = a_{ji}$ *(symmetry)*
- $If\ a_{i,j} = \lambda_1\ ,\ a_{j,k} = \lambda_2 \rightarrow\ a_{i,k} = \lambda\ with\ \lambda \in [0,1]$ Then for any λ should apply $\lambda \geq Min(\lambda_1, \lambda_2)$ *(transitivity)*

5) Every tolerance matrix $\tilde{R}_1$ can be reformed into an equivalence matrix $\tilde{R}$ by at most (n – 1) compositions with itself according to the following Equation 1 (where n is the cardinal number of the set defining $\tilde{R}$) [5]:

$$\tilde{R}_1^{n-1} = \tilde{R}_1 \circ \tilde{R}_1 \circ \cdots \circ \tilde{R}_1 = \tilde{R} \tag{1}$$

6) Based on the equivalence matrix $\tilde{R}$, λ-cut set (or a-cut R_a) R_λ are defined, where $0 \leq \lambda \leq 1$. The R_λ which is a classical set is called lambda intersection of fuzzy set $\tilde{R}$ and is defined as follows:

$$R_\lambda = \{x \mid \mu_A(x) \geq \lambda\} \tag{2}$$

For λ-cut sets of fuzzy relations, the following certain properties are applicable:

- $(\tilde{R} \cup \tilde{S})_\lambda = R_\lambda \cup S_\lambda$
- $(\tilde{R} \cap \tilde{S})_\lambda = R_\lambda \cap S_\lambda$
- $(\bar{\tilde{R}})_\lambda \neq R_\lambda$
- $For\ any\ \lambda \geq \alpha, where\ 0 \leq a \leq 1, then\ R_a \subseteq R_\lambda$

7) Set $[x_i] = \{x_i \mid (x_i, x_j) \in \mathbb{R}\}$, is defined as the equivalent class x_i on a universe of data, X and is contained in a special relation $\tilde{R}$, known as equivalent relation. This class is a set of all elements related to x_i that have the following properties [6]:

- $x_i \in [x_i] \rightarrow (x_i, x_i) \in \mathbb{R}$
- $[x_i] \neq [x_j] \Rightarrow [x_i] \cap [x_j] = \emptyset$
- $\bigcup_{x \in X}[x] = X$

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The first property is that of reflexivity, the second property indicates that equivalent classes do not overlap, and the third property simply expresses that the union of all equivalent classes exhausts the universe X. Hence, the equivalence relation $\tilde{R}$ can divide the universe X into mutually exclusive equivalent classes, i.e.,

$$X \mid \mathbb{R} = \{[x] \mid x \in X\} \tag{3}$$

where $X \mid \mathbb{R}$ is called the quotient set. The quotient set of X relative to $\tilde{R}$, denoted $X \mid \mathbb{R}$ is the set whose elements are the equivalence classes of X under the equivalence relation $\tilde{R}$. The cardinality of $X \mid \mathbb{R}$ (i.e., the number of distinct equivalence classes of X under $\tilde{R}$) is called the rank of the matrix $\tilde{R}$ [5].

2.2 Software

One of the best software for data analysis and for processing matrices is MATLAB (MATrix LABoratory) which is a modern comprehensive mathematical package that is utilized extensively in universities and industry. It is not only an interactive program for numerical computation and construction of graphs, but also provides programmability, which makes it a powerful tool for all scientific fields.

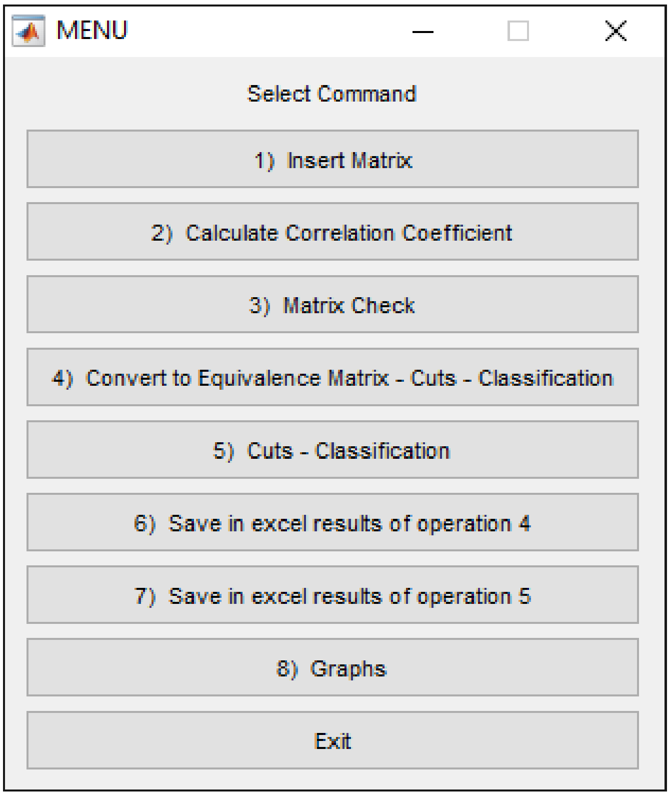


Figure 1. Program menu

The complexity of rainfall data classification requires the construction of a custom software in MATLAB. The software was not only designed for the data under examination but it was generalized for n×n matrices. The software is user friendly, and little knowledge of MATLAB environment is required in order to use it. Figure 1, shows the program menu. The user can choose from a variety of options that helps him to achieve the most accurate possible results depending on the requirements of his problem. Shortly the software: **1)** Accepts the rainfall data in matrix form **2)** Calculates the correlation coefficient obtaining the tolerance matrix. **3)** Check the primary matrix and gives its properties. **4)** Converts tolerance matrix into equivalence matrix obtaining all intermediate matrices. Gives λ-cut sets and classes of the equivalence matrix presents the final classification of data. **5)** Saves the results in excel format. The excel files are named directly from the software depending on the results. **6)** It can create two and three dimensional graphs. **7)** Commands 5-7 have been developed under the assumption that if the primary matrix which is inserted in the software is an equivalence matrix, the user has the possibility to extract the desired results and to save them in excel file. This happens because in the command 4, the properties of the data matrix is checked and in case that is already an equivalence matrix the algorithm stops.

Finally the default number of decimal digits is preset to four but the user can alter this from the MATLAB environment in order to increase the accuracy of the results.

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2.3 Study area and rainfall data

The study area is located in N. Greece and more specifically in the region of Serres. The rainfall stations with their locations and elevations are shown in Figure 2 and values (monthly averages) are shown in Table 1 [7].

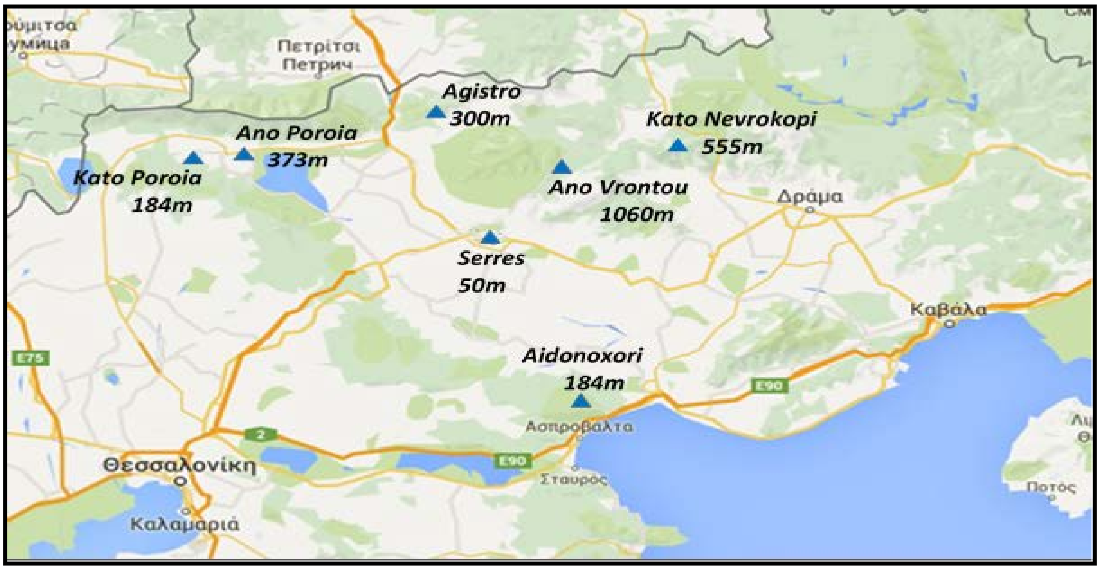


Figure 2. Rainfall stations with corresponding elevations in the region of Serres

Table 1. Monthly averages (mm)

Year	Agistro	Kato Poroia	Ano Vrontou	Aidonoxori	Serres	Ano Poroia	Kato Neurokopi
1929-30	47,6	66,3	65,8	48,8	55,1	50	73,2
1930-31	65,6	78,7	118,9	80,1	55,1	67,8	91,8
1931-32	40,3	62	57	39,5	31,18	55,3	52,1
1932-33	30,8	46,3	52,5	37,4	30	51	52,9
1933-34	45,1	65,4	61,1	44,8	36,8	106,6	52
1934-35	54,1	62,3	73,9	52,6	54,7	68	54,3
1935-36	58,7	86,6	104,4	81	63,2	100,9	75,2
1936-37	60,6	75,6	83,1	60,9	54,6	77,7	78,2
1937-38	55,1	70,7	78,8	51,9	43	60,8	69,1
1938-39	45,9	65,9	79	75,4	48,2	76,2	78,7
1939-40	54,7	68	106,5	50,7	42,4	98,5	80,8
1940-41	47,5	68,1	77,5	55,3	46,2	70,3	64,5

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3. RESULTS

3.1 Tolerance and equivalence matrix

The tolerance matrix of rainfall data in region of Serres has the following form:

$$\tilde{\boldsymbol{R}}_{\boldsymbol{1}} = \begin{bmatrix} 1 & 0.8624 & 0.8414 & 0.6951 & 0.7720 & 0.3548 & 0.7273 \\ 0.8624 & 1 & 0.7696 & 0.7813 & 0.7627 & 0.4852 & 0.6737 \\ 0.8414 & 0.7696 & 1 & 0.7751 & 0.6243 & 0.4363 & 0.8431 \\ 0.6951 & 0.7813 & 0.7751 & 1 & 0.7662 & 0.3389 & 0.7605 \\ 0.7720 & 0.7627 & 0.6243 & 0.7762 & 1 & 0.2128 & 0.6208 \\ 0.3548 & 0.4852 & 0.4363 & 0.3389 & 0.2128 & 1 & 0.1768 \\ 0.7273 & 0.6737 & 0.8431 & 0.7605 & 0.6208 & 0.1768 & 1 \end{bmatrix}$$

where A=Agistro, KP=Kato Poroia, AV=Ano Vrontou, AI=Aidonoxori, S=Serres, AP=Ano Poroia, KN=Kato Neurokopi.
Applying Equation 1 the tolerance matrix $\tilde{R}_1$ is converted into equivalence matrix $\tilde{R}$ after 3 compositions and provides the intermediate matrices:

$$\tilde{\boldsymbol{R}}_{\boldsymbol{1}}^{\boldsymbol{2}} = \begin{bmatrix} 1 & 0.8624 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.8414 \\ 0.8624 & 1 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.7696 \\ 0.8414 & 0.8414 & 1 & 0.7751 & 0.7720 & 0.4852 & 0.8431 \\ 0.7813 & 0.7813 & 0.7751 & 1 & 0.7662 & 0.4852 & 0.7751 \\ 0.7720 & 0.7720 & 0.7720 & 0.7662 & 1 & 0.4852 & 0.7605 \\ 0.4852 & 0.4852 & 0.4852 & 0.4852 & 0.4852 & 1 & 0.4852 \\ 0.8414 & 0.7696 & 0.8431 & 0.7751 & 0.7605 & 0.4852 & 1 \end{bmatrix} \quad \tilde{\boldsymbol{R}}_{\boldsymbol{1}}^{\boldsymbol{3}} = \begin{bmatrix} 1 & 0.8624 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.8414 \\ 0.8624 & 1 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.8414 \\ 0.8414 & 0.8414 & 1 & 0.7813 & 0.7720 & 0.4852 & 0.8431 \\ 0.7813 & 0.7813 & 0.7813 & 1 & 0.7720 & 0.4852 & 0.7751 \\ 0.7720 & 0.7720 & 0.7720 & 0.7720 & 1 & 0.4852 & 0.7720 \\ 0.4852 & 0.4852 & 0.4852 & 0.4852 & 0.4852 & 1 & 0.4852 \\ 0.8414 & 0.8414 & 0.8431 & 0.7751 & 0.7720 & 0.4852 & 1 \end{bmatrix}$$

$$\tilde{\boldsymbol{R}}_{\boldsymbol{1}}^{\boldsymbol{4}} = \tilde{\boldsymbol{R}}_{\boldsymbol{1}}^{\boldsymbol{3}} \circ \tilde{\boldsymbol{R}}_{\boldsymbol{1}} = \tilde{\boldsymbol{R}} = \begin{bmatrix} 1 & 0.8624 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.8414 \\ 0.8624 & 1 & 0.8414 & 0.7813 & 0.7720 & 0.4852 & 0.8414 \\ 0.8414 & 0.8414 & 1 & 0.7813 & 0.7720 & 0.4852 & 0.8431 \\ 0.7813 & 0.7813 & 0.7813 & 1 & 0.7720 & 0.4852 & 0.7813 \\ 0.7720 & 0.7720 & 0.7720 & 0.7720 & 1 & 0.4852 & 0.7720 \\ 0.4852 & 0.4852 & 0.4852 & 0.4852 & 0.4852 & 1 & 0.4852 \\ 0.8414 & 0.8414 & 0.8431 & 0.7813 & 0.7720 & 0.4852 & 1 \end{bmatrix}$$

The matrix $\tilde{R}_1^4 = \tilde{R}$ satisfies the properties of reflexivity and symmetry, but it also satisfies the property of transitivity that transforms it into equivalence matrix $\tilde{R}$.

Continuation of compositions between matrix $\tilde{R}_1^4$ and matrix $\tilde{R}_1$ (Equation 4) will provide the same results [8]. This is another way verifying the final equivalence relation $\tilde{R}$:

$$\tilde{R}_1 \circ \tilde{R}_1 \circ \tilde{R}_1 \circ \tilde{R}_1 \circ \ldots \circ \tilde{R}_1 = \tilde{R} \qquad (4)$$

3.2 λ-cut sets

Here are the λ-cuts of fuzzy equivalence relation $\tilde{R}$, using the Equation 2, for the values
λ = 0.4852, 0.7720, 0.7813, 0.8414, 0.8431, 0.8624, 1:

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$$R_{0.4852}=\begin{bmatrix}1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\\1&1&1&1&1&1&1\end{bmatrix}\quad R_{0.7720}=\begin{bmatrix}1&1&1&1&1&0&1\\1&1&1&1&1&0&1\\1&1&1&1&1&0&1\\1&1&1&1&1&0&1\\1&1&1&1&1&0&1\\0&0&0&0&0&1&0\\1&1&1&1&1&0&1\end{bmatrix}$$

$$R_{0.7813}=\begin{bmatrix}1&1&1&1&0&0&1\\1&1&1&1&0&0&1\\1&1&1&1&0&0&1\\1&1&1&1&0&0&1\\0&0&0&0&1&0&0\\0&0&0&0&0&1&0\\1&1&1&1&0&0&1\end{bmatrix}$$

$$R_{0.8414}=\begin{bmatrix}1&1&1&0&0&0&1\\1&1&1&0&0&0&1\\1&1&1&0&0&0&1\\0&0&0&1&0&0&0\\0&0&0&0&1&0&0\\0&0&0&0&0&1&0\\1&1&1&0&0&0&1\end{bmatrix}\quad R_{0.8431}=\begin{bmatrix}1&1&0&0&0&0&0\\1&1&0&0&0&0&0\\0&0&1&0&0&0&1\\0&0&0&1&0&0&0\\0&0&0&0&1&0&0\\0&0&0&0&0&1&0\\0&0&1&0&0&0&1\end{bmatrix}$$

$$R_{0.8624}=\begin{bmatrix}1&1&0&0&0&0&0\\1&1&0&0&0&0&0\\0&0&1&0&0&0&0\\0&0&0&1&0&0&0\\0&0&0&0&1&0&0\\0&0&0&0&0&1&0\\0&0&0&0&0&0&1\end{bmatrix}$$

$$R_1=\begin{bmatrix}1&&&&&&\mathbf{0}\\&1&&&&&\\&&1&&&&\\&&&1&&&\\&&&&1&&\\&&&&&1&\\\mathbf{0}&&&&&&1\end{bmatrix}$$

3.3 Classification

The universe X contains the seven stations as:

$$X=\{x_1,x_2,x_3,x_4,x_5,x_6,x_7\} \tag{5}$$

Based on the previous results, and Equation 3, Table 3 was constructed which shows the classification of rainfall data depending on λ-cut levels.

Table 3. Classification of seven rainfall stations according to λ-cut levels

λ-cut Level	Classification
0.4852	$\{x_1,x_2,x_3,x_4,x_5,x_6,x_7\}$
0.7720	$\{x_1,x_2,x_3,x_4,x_5,x_7\}[x_6]$
0.7813	$\{x_1,x_2,x_3,x_4,x_7\}[x_5][x_6]$
0.8414	$\{x_1,x_2,x_3,x_7\}[x_4][x_5][x_6]$
0.8431	$\{x_1,x_2\}\{x_3,x_7\}[x_4][x_5][x_6]$
0.8624	$\{x_1,x_2\}[x_3][x_4][x_5][x_6][x_7]$
1	$[x_1][x_2][x_3][x_4][x_5][x_6][x_7]$

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We can express the classification scenario described in Table 3 with a systematic classification diagram, as shown in Figure 3. Also it is shown that for higher value of λ, the classification is more rigorous. That is, as λ gets larger the tendency of classification tends to approach the trivial case where each data point is assigned to its own class.

Figure 4 and Figure 5 were created with the help of a subroutine built in MATLAB and give two-dimensional and three-dimensional representation of the results obtained from the conversion of the tolerance matrix into equivalence matrix.

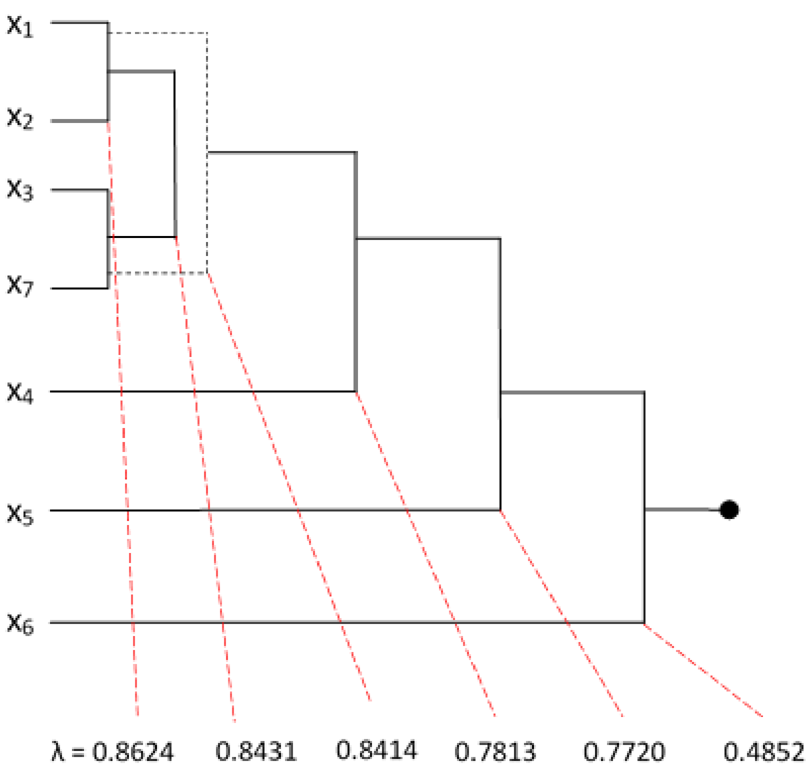


Figure 3. Classification diagram

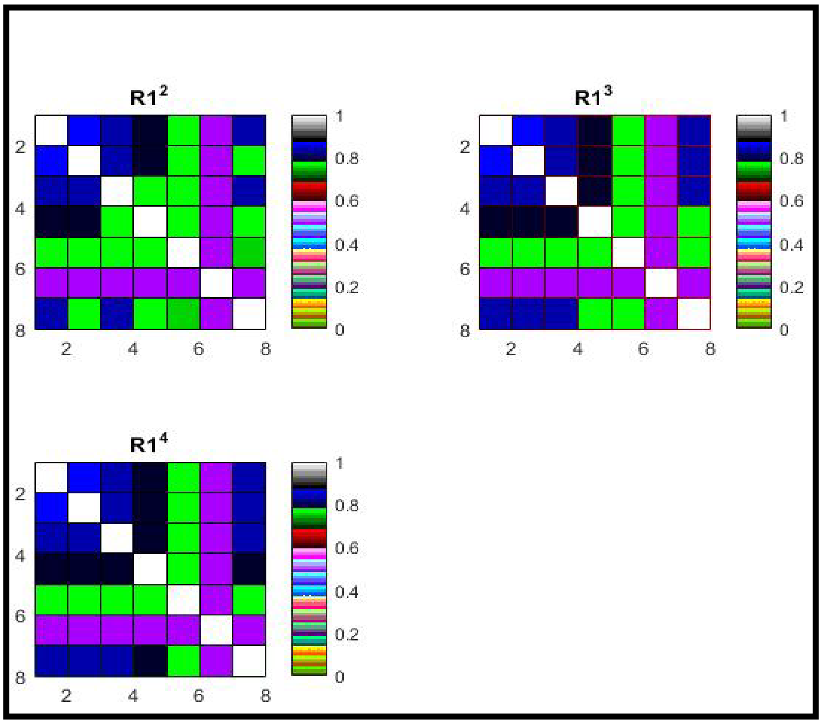


Figure 4. Two-dimensional contours of relations $\widetilde{R}_1^2$, $\widetilde{R}_1^3$,

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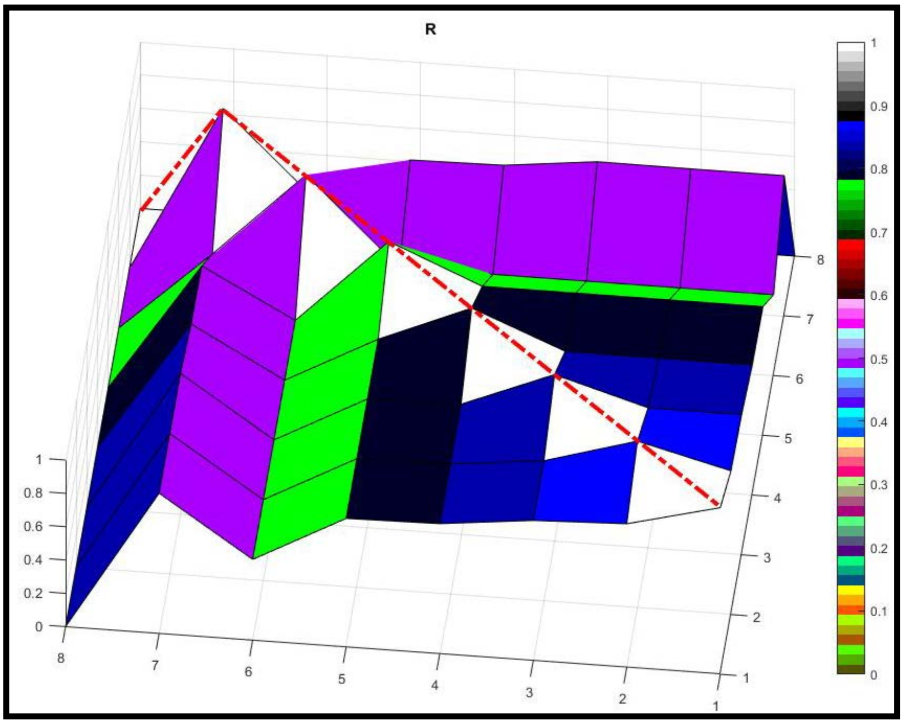


Figure 5. Three-dimensional representation of equivalence relation $\widetilde{R}$

4. CONCLUSIONS

According to the results we can state that the data classification with fuzzy logic can provide answers under a certain degree of confidence in complex problems characterized by ambiguity and uncertainty. To extract the primary matrix (tolerance matrix), the calculation of correlation coefficient of rainfall data was selected. The tolerance relation could also occur through the use of other methods such as the cosine amplitube, max-min method, exponential similarity coefficient, scalar product, geometric average minimum etc. The compositions of the matrices until the tolerance matrix is converted into equivalence matrix, was made by the max-min composition method but it's not the only option for the conversion process; there are other similarity methods such as the max-product etc [5]. Max-min composition and max-product methods are the two most common techniques in the literature. The max-min composition method is the one used by Zadeh in his original paper on approximate reasoning using natural language if-then rules [4].

The best classification obtained, was in the stations of Agkistro and Kato Poroia with a degree of reliability 0.8624, where these stations present acceptable similarity. The elevation difference between the above two stations is around 116 meters. The annual rainfall height received by each position in a region depends on its elevation. It is known that rainfall height increases with elevation. Nevertheless, the classification of rainfall data shows that these two stations have the greatest similarity between all stations with a 0.8624 degree of reliability, which is strong enough. Therefore, although the rainfall stations in regions Agkistro and Kato Poroia have significant elevation difference they have considerable similarity between them. For that reason we can say that the meaning of rain gradient is not valid.

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5. REFERENCES

[1] Zadeh L., 1965. *Fuzzy sets.* Inf. Control, vol. 8, pp. 28-44.

[2] Tzimopoulos C. and Papadopoulos B., 2013. *Fuzzy logic with application in engineering.* Thessaloniki: ZITI. p.627 (in Greek)

[3] Cox E., 1994. *The fuzzy systems handbook, a practitioner's guide to building, using, and maintaining fuzzy systems.* AP Professional, Boston.

[4] Zadeh L., 1973. *Outline of a New Approach to the Analysis of Complex Systems nd Decision Processes.* IEE Trans. Syst. Man, Cybern., vol. 3, pp. 28-44.

[5] Ross J., 2004. *Fuzzy Logic with Engineering Applications.* 2nd ed., John Wiley & Sons, Ltd., p.628

[6] Bezdek J., 1974. *Numerical taxonomy with fuzzy sets.* J. Math. Biol., vol 1, pp. 57-71.

[7] Orphanidou E., 2005. *Strymonas water balance in the Greek region.* Thessaloniki.

[8] Botzoris, G., & Papadopoulos B., 2015. *Fuzzy logic, Application in design and management of engineering projects* . Thessaloniki: Publisher sofia. p.424 (in Greek)

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Sensitivity analysis on tracer transport properties in fractured porous media using COMSOL

I. Bortone[1*], E. Aristodemou[1], R. Bhamidimarri[1], D. Musmarra[2]

[1] School of Engineering, London South Bank University, 103 Borough Rd, London SE1 0AA, London, UK.
[2] Department of Civil Engineering, Design, Buildings and Environment, Second University of Naples, via Roma 29, 81031, Aversa, Italy.
*Corresponding author: Email: bortonei@lsbu.ac.uk

Abstract

Modelling fluid flow in fractured formations is of great interest worldwide, as it can enhance knowledge and understanding of the new exploration technique of hydraulic fracturing for the extraction of shale gas in unconventional reservoirs. This paper is the first step in a series of studies that aim to assess the effect of fractures on both environmental contamination as well as enhanced oil or gas production rates. In particular COMSOL Multi-physics software was implemented in an initial, three-dimensional two-layered porous media geometry, with the objective of testing the COMSOL software for such studies, and introducing the more complex physical processes as well as representing the fractures and faults explicitly within the domain. In this initial study, a fault was represented explicitly, whilst other finer fractures were represented by the increased conductivities within the formation. As expected, preliminary simulations have shown that increasing the formation hydraulic conductivity reduced the breakthrough times, although the presence of the fault only has a significant effect when the shale hydraulic conductivity is low.

Keywords: hydraulic fracturing; groundwater pollution; finite element method; fractured media.

1. INTRODUCTION

Over the last few years, concern related to groundwater contamination of sources due to the new process of hydro-fracking for the extraction of natural gas has increased, with several researchers claiming that deterioration of ground water quality in certain areas is directly linked to this process [1-6]. Hydraulic fracking is aimed at creating several small cracks, or fractures, in underground geological formations to allow the natural gas to flow into a well-bore without pumping and thereby increasing the production of it [2]. Once the hydraulic process is completed, the initial fracturing fluids, together with the fluids displaced from the geological formations, rise to the surface and are collected. However, the method is still controversial, despite its many applications in the USA and Canada, as there are risks associated with both public health and environmental effects such as contamination of groundwater aquifers and triggering of small earthquakes [2]. To fracture the formation, in fact, large amount of special fracturing fluids are injected at high pressures down the well-bore and into the formation, and the amount of injected fluid that returns to the ground surface, after fracking is applied, is lower than 40% [3]. Some studies showed that fracking fluid has been found in aquifers [4-6] demonstrating that the potential for various forms of water pollution exists. In particular, in Pennsylvania, possible contamination of drinking groundwater associated with shale gas extraction has been reported from Marcellus shale [4,5], as it was found that methane concentrations were substantially higher closer to shale gas wells than the regional natural concentration. In addition, other studies from some researchers at the University of Texas at Arlington [6] revealed elevated levels of arsenic and other heavy metals in private drinking water wells near natural gas wells in North Texas' Barnett Shale. Samples from 100 wells, both inside and

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outside of the Barnett Shale were analysed and arsenic was found in 99 of the 100 wells with levels significantly higher in active gas extraction areas.

Studying the fluid flow and contaminant transport in such environments is a complex area of research as it requires representation of the high formation heterogeneities, directional dependence, multi-component nature and multiscale behaviour, being the oil and gas reservoirs crossed by multiscale fractures/faults [7]. When faults are present, the potential impact of shale gas mining increases the potential risk of it, as in those cases advective transport and two potential pathways through formation media and fractures allow the transport of contaminants from the fractured shale to nearby aquifers [8,9]. To model these systems, simplified models have been developed [7]. Myers [8] discussed the possible pathways from hydraulic fractured Marcellus shale to the fresh water aquifer in Pennsylvania via a two layered system. With interpretative modelling using Modflow and by considering different conductivities for each layer, he showed that advective transport could require up to tens of thousands of years to move contaminants to the surface, and also that fracking the shale could increase the velocity transport and consequently reduce that transport time to tens or hundreds of years. In addition, he obtained that by adding conductive faults or fracture zones, as found throughout the Marcellus shale region, the travel time could further reduce to less than 10 years. However his results were questioned as some of them had some calculation errors [10,11].

This paper proposes to provide a better understanding of the fluid flow and transport of contaminants in fractured reservoirs via 3D finite element modelling simulations, by considering Myers simulations [8]. A two layered system and the effect of a fault were tested, as a first step in a series of studies with the objective to assess one of the largely unexamined issues of slow contamination of shallow groundwater due to hydraulic fracturing at depth via fluid and contaminant migration along conductive cracks. Preliminary simulations were replicated using COMSOL Multi-physics® software by analysing the steady state travel time for some tracer through layers of sandstone and shale. A sensitivity analysis on tracer transport in porous media with and without a fault was carried out aimed at quantifying the effect of the hydraulic properties of the porous media (i.e. hydraulic conductivities) as well as the effect of a fault, in terms of contamination transport timescales. Results showed that different formation conductivities have an effect on the overall fluid flow and hence a consequent expected effect on the concentration time of to reach the groundwater.

2. MATERIALS AND METHODS

2.1 Transport modelling

Time evolution of solute transport in porous media can be described via the advection-dispersion equation (Equation 1)[12]:

$$\underline{\textit{Advection-Dispersion Equation}}:\quad \theta\frac{\partial C}{\partial t}+\nabla[-\theta D_h\nabla C+\underline{u}C]=0 \qquad (1)$$

where C is the groundwater contaminant concentration, t is the time, D_h is the hydrodynamic dispersion tensor, $\underline{u}$ is the pore water flow velocity vector, and θ is the effective porosity. The hydrodynamic dispersion tensor, D_h , is expressed as the sum of the tensor of mechanical dispersion, D_m, and the coefficient of molecular diffusion, D_{iff}, (a scalar), as better described by Konikow and Grove [13]. Darcy equation (Equation 3) can be used to evaluate the pore water flow velocity vector $\underline{u}$, which depend on the hydraulic conductivity, K, and on the hydraulic head gradient ∇h (where h is the hydraulic head) and is written as follows:

$$\underline{\textit{Darcy's Equation}}:\quad \underline{u}=K\cdot\nabla h \qquad (2)$$

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The initial and boundary conditions for both concentration (Equation 3) and hydraulic head fields (Equation 4) used, were as given further below.

Concentration initial condition

$$C(x,y,z)=0 \qquad t=0$$

Concentration boundary conditions (3)

$$C(x,y,0)=C_0 \qquad t>0$$

$$-n\cdot[-\theta D_h \nabla C+uC]=0 \qquad \begin{matrix} x=0,\ x=X & \forall y \forall z \forall t \\ y=0,\ y=Y & \forall x \forall z \forall t \end{matrix}$$

$$-n\cdot[-\theta D_h \nabla C]=0 \qquad z=Z \quad \forall x \forall y \forall t$$

Hydraulic head initial condition

$$h(x,y,z)=0 \qquad t=0$$

Hydraulic head boundary conditions (4)

$$h(x,y,0)=h_1 \qquad z=0 \quad \forall x \forall y \forall t$$

$$h(x,y,Z)=h_2 \qquad z=Z \quad \forall x \forall y \forall t$$

$$-n\cdot \underline{u}=0 \qquad \begin{matrix} x=0,\ x=X & \forall y \forall z \forall t \\ y=0,\ y=Y & \forall x \forall z \forall t \end{matrix}$$

In Equations 3 and 4, n is the unit vector normal to the boundary, while X, Y and Z represent the size of the computational domain along the x-, y- and z-directions and h_1 and h_2 are the hydraulic head values at the bottom and at the top of the model respectively. The equation system (1)-(2), with the related initial and boundary conditions (3) and (4) were solved numerically via finite element method by using COMSOL Multi-physics®.

2.2. Numerical methods and parameter values

Simulations were conducted with COMSOL, a finite element simulator of subsurface flow considering a multi-physic environment. The case study examines the vertical transport of contaminants throughout a Marcellus shale region of thickness 30m (H_{sh}) and the above sandstone layer of thickness 1470m (H_{ss}) [8] in presence and absence of a fault (Figure 1a and Figure 1b). The fault was considered as vertical column having much higher conductivity than the surrounding media, as shown in Figure 1(b). Figure 1(c) represents the computational mesh used by COMSOL for the simulations.

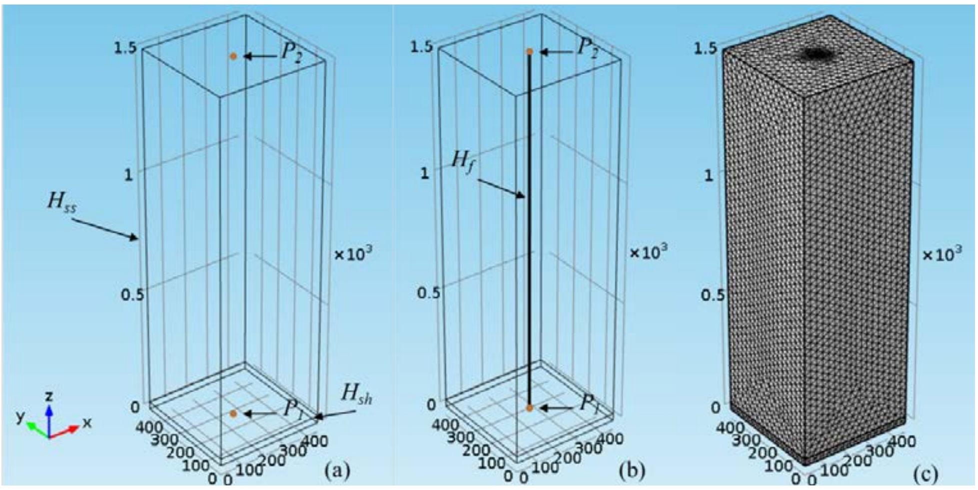


Figure 1. Model representation without fault (a), with fault (b) and computation mesh (c).

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The mesh was a physics-controlled mesh of 286055 elements with minimum quality of 0.1049m and average quality of 0.7484m. The base case values and parameters both for the shale and the sandstone layers and the fault are presented in Table 1. The model simulated a vertical flow with a gradient of 0.019 over the profile.

Table 1. Main characteristics of the model and of the fault

Parameter		**value**	**units**
Model width	X	450	[m]
Model depth	Y	450	[m]
Model height	Z	1500	[m]
Shale thickness	H_{sh}	30	[m]
Sandstone thickness	H_{ss}	1470	[m]
Aquifer bottom hydraulic head	h_1	1580	[m]
Aquifer top hydraulic head	h_2	1550	[m]
Piezometric gradient	J	0.019	[m m^{-1}]
Porosity	θ	0.1	[-]
Sandstone hydraulic conductivity	K_{ss}	0.01-10	[m d^{-1}]
Shale hydraulic conductivity	K_{sh}	0.0001-0.1	[m d^{-1}]
Longitudinal dispersivity	α_z	10	[m]
Transverse dispersivity	α_x, α_y	1, 0.1	[m]
Molecular diffusion coefficient	D_{iff}	10^{-8}	[m^2 s^{-1}]
Fault parameters			
Fault width	X_f	6	[m]
Fault depth	Y_f	6	[m]
Fault thickness	H_f	1470	[m]
Fault hydraulic conductivity	K_f	0.1-10	[m d^{-1}]

Equivalent permeabilities for each layers were considered taking into account both the fissures and matrix media [8]. Differently to Myers [8], the dispersion and diffusion effects were also taken into account with a longitudinal dispersivity, α_z, in the direction of flow, equal to 10m, transverse dispersivities, α_x, α_y, equal to 1m and 0.1m respectively [9], while the diffusion coefficient, D_{iff}, was set equal to 10^{-8} m^2 s^{-1}.

Table 2. Sensitivity analysis scenarios with and without a fault

No fault			
		K_{ss} [m/d]	**K_{sh} [m/d]**
Scenario 1	***S1-1***	0.1	0.0001
	S1-2	0.1	0.001
	S1-3	0.1	0.01
Scenario 2	***S2-1***	0.01	0.1
	S2-2	0.1	0.1
	S2-3	1	0.1
Scenario 3	***S3-1***	0.1	0.01
	S3-2	1	0.01
	S3-3	10	0.01
Scenario 4	***S4-1***	1	0.0001
	S4-2	1	0.001
	S4-3	1	0.01

With fault				
		K_{ss} [m/d]	**K_{sh} [m/d]**	**K_f [m/d]**
Scenario 5	***S5-1***	0.01	0.0001	1
	S5-2	0.01	0.001	1
	S5-3	0.01	0.01	1
Scenario 6	***S6-1***	0.1	0.0001	1
	S6-2	0.1	0.001	1
	S6-3	0.1	0.01	1
Scenario 7	***S7-1***	0.1	0.01	0.1
	S7-2	0.1	0.01	1
	S7-3	0.1	0.01	10

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2.3 Sensitivity analysis

Because hydraulic fracking increases the permeability of the targeted shale and because of the uncertainty of that parameter due to the fracking process itself, a sensitivity analysis was carried out. In particular, the effect of hydraulic conductivity for both sandstone layer, K_{ss}, and shale layer, K_{sh}, and fault, K_f, were investigated, based primarily on Myers [8] scenarios, and the most significant cases are reported in Table 2. These considered a range of conductivities for the sandstone layer, the shale layer and the fault respectively, by varying them from 0.0001 to 10m d^{-1} and by comparing the consequence of the presence of fault. In particular, 7 scenarios are presented: in *Scenario 1* and *Scenario 4*, K_{ss} was maintained constant by changing K_{sh}, while in *Scenario 2* and *Scenario 3*, K_{ss} was changed between 0.01 and 10m d^{-1}. *Scenarios 5*, *6* and *7* simulated instead the presence of a fault where K_f was maintained constant equal to 1m d^{-1} for both *Scenario 5* and *Scenario 6* and it was changed for *Scenario 7*, ranging from 0.1 to 10m d^{-1}, while K_{sh} and K_{ss} were equal to 0.01 and 0.1m d^{-1} respectively. In particular *Scenario 1* and *6* compare the same sandstone and shale conductivities range with and without the fault with K_f=1m d^{-1} .

3. RESULTS AND DISCUSSION

In order to understand the effect of the fault, two probes, P_1 and P_2, placed in the centre of the horizontal-cross section, where also the fault is located, with P_1 being at the top of the shale (x=225,y=225,z=30m), whilst P_2 being at the top of the sandstone (x=225, y=225, z=1500m) (Figure 1) were considered. Outlet fluxes and concentrations over the time were detected for all scenarios, both with and without a fault. Table 3 shows the fluxes at the top of the shale (at probe P_1) with and without the fault.

Fluxes at probe 2 are not shown as the values are similar to the values at probe P_1. In addition, as shown in Table 3, by comparing *Scenarios 1* and *6* flux values (at probe P_1), the presence of a the fault did not significantly change the overall model flux.

In Figure 2 the simulated transport times for the maximum concentration values at the top of the model (probe P_2) for varying shale, sandstone and fault conductivities (K_{ss}, K_{sh}, K_f) are reported. Figure 3 shows the outlet concentrations over time, at the probe P_2 for *Scenario 1* (no fault case) and *Scenario 6* (with the fault), whilst Figure 4 shows the results for *Scenario 7* which looks at the variation of the fault conductivity, K_f.

Table 3. Fluxes and transport time for probes P_1 with and without a fault

No fault			With fault		
		Flux P1 [kg/m²s]			**Flux P1 [kg/m²s]**
Scenario 1	***S1-1***	1.103E-06	***Scenario 5***	***S5-1***	7.807E-07
	S1-2	7.765E-06		***S5-2***	1.988E-06
	S1-3	1.961E-05		***S5-3***	2.349E-06
Scenario 2	***S2-1***	2.356E-06	***Scenario 6***	***S6-1***	1.102E-06
	S2-2	2.314E-05		***S6-2***	7.762E-06
	S2-3	1.961E-04		***S6-3***	1.963E-05
Scenario 3	***S3-1***	1.961E-05	***Scenario 7***	***S7-1***	1.961E-05
	S3-2	7.765E-05		***S7-2***	1.962E-05
	S3-3	1.103E-04		***S7-3***	1.971E-05
Scenario 4	***S4-1***	1.151E-06			
	S4-2	1.103E-05			
	S4-3	7.765E-05			

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Cases without fault

Scenario 1: Increasing the conductivity of shale, K_{sh}, as shown in Table 3, there is an increase of flux by a factor of 10 almost.

Scenario 2: A relatively high shale conductivity (K_{sh}=0.1m d^{-1}) has a marked effect on the flux value, as well as the transport time, especially when the sandstone conductivity is also high (K_{ss}=1m d^{-1}).

Scenario 3: This has a lower shale conductivity (K_{sh}=0.01m d^{-1}) than *Scenario 2*, but has increased sandstone conductivities, K_{ss}, up to the value of 10m d^{-1}, affecting the flux value at the top of shale (P_1), although not as much as expected for the high conductivity value of 10m d^{-1}, as well as the transport time.

Scenario 4: Same shale conductivities as in *Scenario 1*, but increased sandstone conductivity, K_{ss} (hence fractures in sandstone). Increasing K_{ss} by a factor of 10 (from 0.1m d^{-1} to 1m d^{-1}) has a greater effect at the higher shale conductivities, while for the lower K_{sh} the effect is minimal.

All scenarios emphasise the effect of one media to the other and when K_{sh} is very low, transport time is quite long and not sensitive to K_{ss}. The shortest simulation time detected was for *Scenario 2* (*S2-3*) when K_{ss} and K_{sh} are respectively 1 and 0.1m d^{-1}.

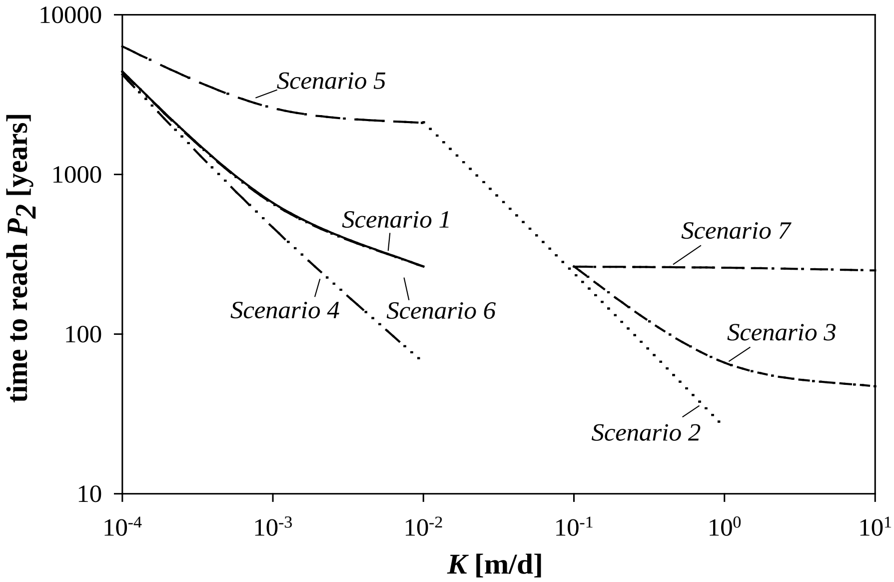


Figure 2. Concentration transport time over P_2 for varying shale, sandstone and fault hydraulic conductivities, *K*, for all scenarios.

Cases with fault

In order to see the effect of the presence of fractures, a number of simulations in presence of a fault were also considered and compared with the equivalent cases without a fault. In particular, *Scenarios 1* and *6* were considered, as in all cases the properties of the shale and sandstone were the same with the only difference of the fault in *Scenario 6*. The results showed that the flux values between the fault and no-fault cases were very much the same, especially when the shale and sandstone conductivities were relatively “high” (0.1m d^{-1} and 0.01m d^{-1} respectively), and similarly for the transport times (Figure 2). However, when K_{sh} was low (0.0001 m d^{-1}) the present of the fault had an effect, not on the final flux value, but on the transport time. This can also be seen in Figure 3, where a comparison between the no-fault and with-fault cases is represented.

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These results led to a set of simulations looking at the effect of the fault conductivity, K_f, by increasing it to the value of 10m d^{-1} in *Scenario 7*. From Figure 4, the breakthrough time is much smaller for the higher conductivity of 10m d^{-1} (< 100 years) whilst for fault conductivities, K_f, of 1m d^{-1} and 0.1m d^{-1} the breakthrough times are higher than 200 years. Similarly, the time required for the concentrations to become 50% of the maximum concentration is higher (> 200 years) when the fault conductivities are lower (*S7-1* and *S7-2*).

Results about the timescales from the cases without a fault (*Scenarios 1-4*) showed to be congruent to Myers [8], apart from one case, which was already disputed by Cohen et al. [11]. Cohen et al. [11] also disputed Myers's flux values; our simulated fluxes were in agreement with theirs [11]. Results obtained with a fault (*Scenarios 5-7*) showed to be not congruent with Myers [2], instead, who declared that the travel time could further reduce to less than 10 years, which does not seem to happen in our simulations.

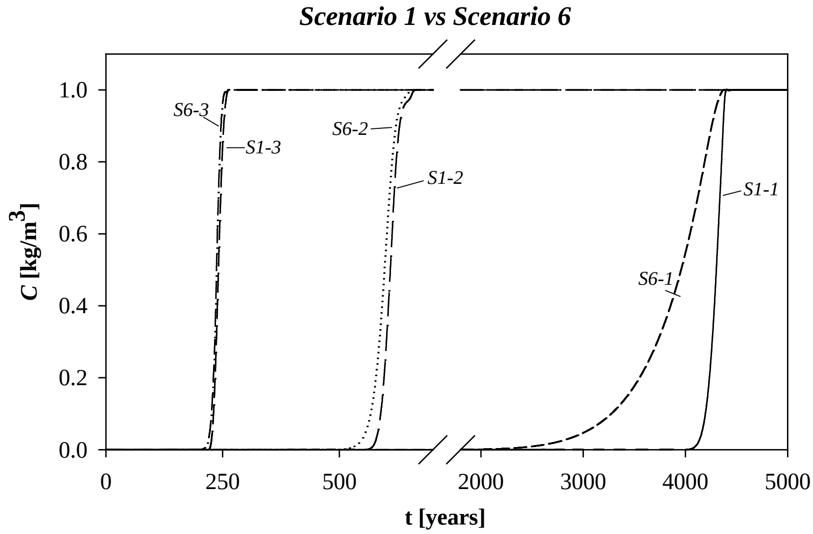


Figure 3. Outlet concentrations over time at point P_2 for scenarios with fault (*Scenario 6*) and without fault (*Scenario 1*) for varying hydraulic shale and sandstone conductivities and a fixed fault conductivity K_f = 1m/d.

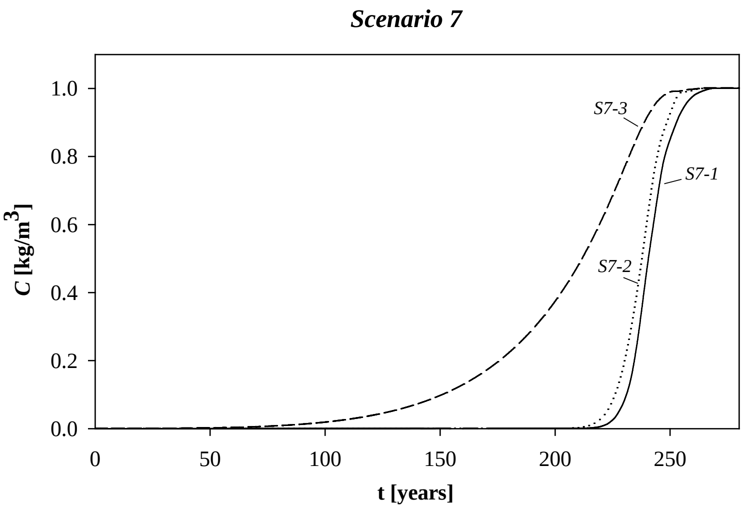


Figure 4. Outlet concentrations over time at probe P_2 of the model for *Scenario 7*, with a fault by varying the fault conductivity K_f.

4. CONCLUSIONS

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In this paper a sensitivity analysis on solute transport in fractured porous media with and without a fault was carried out. In particular COMSOL Multi-physics software was implemented in an initial, simple two-layer (shale-sandstone) system, represented in three dimensions aimed at quantifying the effect of different hydraulic conductivities on the pollution transport timescales as described in Myers [2]. The aim is to provide a first step in a series of studies aiming at assessing the effect of fractures on both environmental contamination as well as enhanced oil or gas production rates and better understanding the fluid flow and transport of substances in porous media when fractures/faults are present.

Results showed that the presence of a fault does not seem to influence the breakthrough time of concentrations, when the shale conductivity is relatively high, while an influence was noticed for low shale conductivity values (K_{sh}=0.0001 m d^{-1}), as well as by increasing the fault conductivity.
Further simulations representing single fractures explicitly within the COMSOL software on multiple scales will be carried out, as well as considering the effect of different dispersivities. The impact of multiphase flow on contaminant transport will also be assessed taking into account both the temperature influence and more complex hydrological conditions, in order to estimate, in a more reliable way, fluid migration and solute transport in subsurface environments regards to shale gas reservoirs.

References

[1] DiGiulio D.C., Wilkin R.T., Miller C., Oberly G., 2011. DRAFT: Investigation of Ground Water Contamination near Pavillion, Wyoming. Ada, Oklahoma: U.S. Environmental Protection Agency, Office of Research and Development.

[2] U.S. EPA, 2012. *Study of the potential impacts of hydraulic fracturing on drinking water resources*, EPA, 601/R-12/011.

[3] Alleman D., 2011.Water used for hydraulic fracturing: Amounts, sources, reuse, and disposal. In Hydraulic Fracturing of the Marcellus Shale, National Groundwater Association short course. Baltimore, Maryland.

[4] Osborn S. G., Vengosh A., Warner N. R., Jackson R. B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences*, **108(20)**, 8172–8176.

[5] Warner, N. R., Kresse, T. M., Hays, P. D., Down, A., Karr, J. D., Jackson, R. B., Vengosh, A., 2013. Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. *Applied Geochemistry*, **35**, 207−220.

[6] Fontenot, B.E., Hunt L. R., Hildenbrand Z. L., Carlton D. D., Oka H., Walton J. L., Hopkins D., Osorio A., Bjorndal B., Hu Q., Schug K. A., 2013. An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale Formation. *Environmental Science & Technology*, DOI: 10.1021/es4011724.

[7] Henn N., Quintard M., Bourbiaux B., Sakthikumar S., 2004. Modelling of Conductive Faults With a Multiscale Approach. *Oil & Gas Science and Technology*, **59**, 197-214.

[8] Myers T., 2012. Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water*, **50(6)**, 872–882.

[9] Gassiat, C., Gleeson T., Lefebvre R., McKenzie J., 2013. Hydraulic fracturing in faulted sedimentary basins: Numerical simulation of potential contamination of shallow aquifers over long time scales. *Water Resources Research*, **49**, 8310–8327.

[10] Saiers, J., Barth E., 2012. Potential contaminant pathways from hydraulically fractured shale aquifers. *Ground Water*, **50(6)**, 826–828.

[11] Cohen H., Parratt A., T., Andrews C. B., 2013. Potential contaminant pathways from hydraulically fractured shale to aquifers. *Groundwater*, **51(3)**, 317–319.

[12] Bear, J., 1979. *Hydraulics of Groundwater*, McGraw-Hill, New York.

[13] Konikow, L.F., Grove, D.B., 1977. *Derivation of equations describing solute transport in ground water*. US Geological Survey, Water-Resources Investigations Report 77-19.

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Climate data processing, assessment and corrective methods

S. Sotiriadou, Z. Mallios*

Division of Hydraulics and Environmental Engineering, Department of Civil Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
*Corresponding author: Email: zmallios@civil.auth.gr

Abstract

Climate data almost always comprehend disunions, which are considered as bias and may occur due to many factors, such as the source of these data (land surface, sea surface, satellites) or the way and the conditions of the data recording (type of measuring instruments, distance between measuring instrument and land surface etc.). The effort to deal with the problems caused by such bias, drove to the development of many bias detection methods as well as many data correction methods. The aim of this paper is to review and compare all the different available methods that are easily implemented and applied to climate data in order to correct them, and also to assess the impact of the bias correction on the final corrected data reliability. There many corrective methods, able to correct from the simplest to the most advanced disunion, which are based rather on statistic and much less on experimental methods.

Keywords: climate data; bias correction; methods review; statistic methods.

1. INTRODUCTION

Climate data time series is an important basis on which climate change research depends, as they provide useful information about many climate variables. At first, the recording of such data occurred only by instruments on the land surface, but nowadays the recording network has been expanded also on sea surface and satellites.

Concerning the study and analysis of climate change but also the weather phenomena, especially the extreme ones, a collection of recording data worldwide has been made and a few global or local databases have been resulted. The largest global databases are: the GHCN Monthly Version 3 (Global Historical Climatology Network- Monthly) [1] of NCDC (National Climatic Data Center) of NOAA (National Oceanic and Atmospheric Administration) of USA, which contains monthly temperature, precipitation and atmospheric pressure data by thousands of ground stations worldwide, and the HadCRUT4 [2], which is a global temperature database, providing gridded temperature anomalies across the world, developed by Climate Research Unit (University of East Anglia) in conjunction with Hadley Centre (UK Met Office) and combines land (CRUTEM 4) with ocean data (HadSST3). In Greece, the largest climate database has been developed by the National Observatory of Athens [3], which contains historical climate time series of 150 years about Athens and recent climate data by more than 250 weather stations in Greece.

The fact that climate data is used for the study and analysis of climate change, makes it obvious and necessary that this data should be accurate and complete. A climate time series is considered homogenous if the variations that occur are caused only by variations in weather and climatic conditions. However, time series are often affected by many non-climatic factors which make these time series unsuitable and non-representative for the climatic changes. Thus, these non-climatic factors may introduce artificial discontinuities, called inhomogeneities, in time series. Examples of such non-climatic factors are: errors in recording instruments, changes in measurement conditions, relocation of a station, changes in the formula for calculation of variable mean, use of different

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daily times in the calculation of daily mean temperature etc. There are three main types of inhomogeneities: point errors, shifts in the mean and trends [4].

Nowadays, there are several methods that have been developed in order to detect and correct every possible inhomogeneity in climate data. These methods are based on the statistical approach of time series and may have many different characteristics.

2. INHOMOGENEITIES DETECTION AND CORRECTION METHODS

The continuous research and development on the homogenization of climate data time series has led to the development of many homogenization methods with different characteristics. The decision of which homogenization method would be better and more efficient to be used every time is a very important process that requires a quality control before the homogenization process, so that the inhomogeneities in climate data would be reduced and corrected effectively and the time series reach the necessary continuity and good quality. The different characteristics of each homogenization method are analyzed in the following sections.

2.1 Direct and indirect homogenization methods

For some authors, direct methods are those that are only based on metadata and subjective judgements [5], while others have defined direct methods as mathematical algorithms that are able to detect multiple breakpoints in a direct way [6]. In this paper, the definitions of direct and indirect methods are provided by [7] and [8]. For these authors, direct methods include the use of metadata, the analysis of parallel measurements and statistical studies of instrument changes. The indirect methodologies consider the use of single station data (absolute approaches), the development of reference time series (relative approaches), and include both subjective and objective methods.

In other words, direct methods aim to keep the climate time series homogeneous by anticipating changes in and around a meteorological station and limit their impact on climate data homogeneity [8]. Direct methods rely on the use of metadata information, which can provide precise knowledge of any change that happened to the station and its conditions, as well as when a discontinuity occurred and what caused it.

On the other hand, indirect methods use a variety of statistical and graphical techniques to test the homogeneity and adjust the data series [8]. Indirect methods are distinguished between subjective and objective approaches. Subjective methods rely mostly on experts' judgments, while objective detection methods can be applied in automatic way, without any subjective element.

According to [7] and [8], objective methods contain the group of absolute and relative approaches, which will be analyzed in the following section.

2.2 Absolute and relative homogenization methods

Regarding the use of additional (reference) climate time series, the homogenization methods are distinguished between absolute and relative methods. Absolute methods consider only the climate time series of a single station, the candidate station, to identify and adjust inhomogeneities, so the statistical tests are applied to each independent station. Relative methods use data from the surrounding stations (reference stations) to homogenize the candidate station.

While both approaches are worthwhile and valid, they both have drawbacks. With the absolute method it is difficult to determine if a change-point is caused by climatic change factors. To overcome this problem, metadata support from station history information is essential for evaluating the breaks detected. This is the reason why some authors, like [9], advising that absolute homogenization methods are to be avoided in favor of relative methodologies. The relative methods attempt to isolate the impacts of non-climate factors, which assumes that in a geographical area the climate patterns are identical and all sites observed in the region reflect the same pattern. Therefore,

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the same climate data collected from all sites of the region should be highly correlated and have similar variability, but different conversion factors and random sampling variability. However, it will also cause problem if the observation stations and other elements change at the same time [5].
Another issue is how to select surrounding stations that are free from artificial discontinuities in order to be used as reference stations. According to [10], a good reference series should be homogeneous and highly correlated with the candidate series. Although the use of reference series has some flaws, most of the studies on homogeneity are still based on the effective use of the reference series, taking the following four steps: 1. metadata analysis and basic quality control, 2. establishment of the reference series, 3. change-point detection, 4. data adjustment. The ability of the test can be improved if the effective reference series are used [5].

2.3 Multiple breakpoint techniques

One of the fundamental problems of homogenization is the fact that usually more than one breakpoint is present in the candidate time series [11]. The majority of the statistical homogenization methods deals with this problem by applying single-breakpoint techniques multiple times [12]. The disadvantage of this segmentation process is that the same test applied several times on the same observations can increase the risk of false detection [13].
Multiple breakpoint methods are those that detect and correct multiple change-points jointly, and not step-by-step. Recent studies indicate that these are the most effective detection procedures [14].

3. STATISTICAL HOMOGENIZATION METHODS

In this section the main statistical homogenization methods that are used to correct the inhomogeneities in every kind of time series, not only in climate data time series, are described. These methods could be classified in four categories based on their characteristics: non-parametric tests, classical tests (traditional techniques), regression models and Bayesian approaches [12].

The most common non-parametric tests used for homogeneity testing are:

- Von Neumann ratio test [15]
- Wald-Wolfowitz runs test [16]
- Mann-Kendall test [17, 18]
- Wilcoxon-Mann-Whitney [19, 20]
- Kruskal-Wallis test [21, 22]
- Pettitt’s test [23]

Statistical classical tests are those which correspond to traditional homogenization techniques. The most important are:

- Double mass analysis [24]
- Craddock’s test [25]
- Bivariate test [26]
- Buishand Range test [27]

The three methods using regression models are:

- Two-phase regression [28]
- Multiple linear regression [29]
- Method of cumulative residuals [30]

Bayesian methods have a different approach from classical techniques. Through a prior distribution, the Bayesian approach acquires some knowledge about the climate variable being studied. The main methods of this category are:

- Bayesian multiple change-point detection in multiple linear regression [31]
- Bayesian change-point in multiple linear regression [32]
- Bayesian change-point algorithm [33]

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- Bayesian multiple change-point and segmentation algorithm [34]
- Change-point detection algorithm [35]
- Bayesian Normal Homogeneity Test [36]

4. HOMOGENIZATION PROCEDURES

There are some techniques that were directly proposed as methods for the homogenization of climate data time series. These are:

- SNHT- Standard Normal Homogeneity Test [37]
- SNHT with trend [38]
- MASH- Multiple Analysis of Series for Homogenization [39]
- PRODIGE [40, 41]
- Geostatistical simulation approach [42]
- ACMANT- Adapted Caussinus- Mestre Algorithm for homogenizing Networks of Temperature series [43]
- ACMANT2 for homogenizing daily and monthly precipitation series [44]

The Standard Normal Homogeneity Test (SNHT) [37] is one of the most popular and robust homogenization methods for climatic variables. The application of SNHT begins with the creation of a composite (ratio or difference) series between the station values and some regional reference values assumed homogeneous. This composite series is then standardized. At a given moment, averages are calculated for the previous and the following period of that composite series. If the difference between those averages meets a critical value, a shift is inferred to exist at that moment, and the series is said to be inhomogeneous. Later, [38] improved the SNHT method to extend its detection to trends as well.

The Multiple Analysis of Series for Homogenization (MASH) [39] was one of the first multiple breakpoint techniques. Currently, it is based on mutual comparisons of series within the same climatic area, and does not assume a homogenized reference series.

A new multiple breakpoint technique named PRODIGE, proposed by [40, 41], is based on penalized likelihood methods. The methodology uses a pairwise comparison for preselecting a set of accidents, which are considered within the framework of a multidimensional approach. This method is based on the principle that the series is reliable between two change-points.

The Geostatistical simulation approach proposed by [41] can be summarized as the Direct Sequential Simulation (DSS) algorithm, generates realizations of the climate variable through the resampling of the global probability density function (pdf), using the local mean and variance of the candidate station, which are estimated through a spatiotemporal model.

Adapted Caussinus–Mestre Algorithm for homogenizing Networks of Temperature series (ACMANT), proposed by [43], is a relative homogenization technique applicable to monthly temperature series. Recently, [44] proposed a new unit for the homogenization of monthly or daily precipitation series, ACMANT2. This new version takes into consideration the climatic regions of snowy winters, by making a distinction between rainy season and snowy season and by searching the seasonal inhomogeneities with bivariate detection [12].

Both statistical homogenization methods described in the section 3 and homogenization procedures described in this section based on inhomogeneities detection and correction methods that are analyzed in section 2. In [12] there is a detailed table with all the homogenization methods and their characteristics. For example, the SNHT method, one of the most common homogenization method for climate data time series, which uses annual or monthly data, is a relative homogenization method and is usually applied to composite reference series. On the other hand, MASH method is an objective homogenization method which uses annual, seasonal, monthly or daily data and is able to deal with multiple inhomogeneous references.

5. HOMOGENIZATION SOFTWARE

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In recent years, some of the homogenization methods already described in the previous sections were developed into software, in order to diminish the time consumed during the homogenization process and to minimize the interaction of users. According to [12], some of the most popular homogenization software packages are:

- Climatol [45]
- RHTest [46]
- AnClim and ProClimDB [47, 48]
- USHCN [49]
- HOMER [50]

All these programs despite the ease and the speed that offer to the homogenization process, have some drawbacks, therefore it is very important that they will be upgraded and improved.

6. CONCLUSIONS

Nowadays, the importance of having accurate and precise climate data is fundamental for the complete study and research on climate change, which undeniably has a great impact on human and generally on Earth. For this reason, several homogenization methods have been developed. Their aim is to detect and correct any inhomogeneities that occur in climate data time series. This procedure is a very difficult and complex task. A really important thing in the homogenization process is the availability of historical information of the stations. This paper highlights the most significant and popular homogenization methods, the statistical homogenization tests that are used and some homogenization software packages that have been developed.

Some general conclusions enunciated by the previous analysis are the following:

- Relative homogenization methods improve the homogeneity of climate data, while absolute homogenization techniques have the potential of making the data even more inhomogeneous.
- The selection of reference stations for the relative homogenization methods should be very careful process and it should be considered not only the distance and the correlation, but also the climatic and geomorphological characteristics
- Techniques that detect and correct multiple breakpoints and work with inhomogeneous references generally perform better than other methods.
- Collecting and processing of metadata should be enhanced. Important metadata which is used to evaluate the homogeneity of the surface climate series includes station relocation, instrument changes and destruction, the new statistical equations, changes of the surrounding environment, the times of the observation. Detailed metadata can provide necessary and objective support and will promote the development of homogenization research.
- A homogenization method is considered efficient when is able to overcome two problems: the fact that nearby stations are also inhomogeneous, and the existence of more than one irregularity within the time series. Depending on the used techniques, some homogenization methods can be more appropriate for a specific climate variable (e.g. temperature), while others can only be used at a given time scale resolution (e.g. monthly data). In order to assess their efficiency, numerous comparison exercises are described in the literature. Comparison studies also proved the difficulty of indicating which method is the most efficient. The ultimate goal of homogeneity research is to establish procedures of data products that can be regularly updated and used in operational procedures. Hence, these need to be continuously improved by comparing different homogeneity methods currently being used.
- Homogenization algorithms developers should invest more effort into making their software easy to use and to include relevant warnings [12], as the automatic process has many

advantages, such as objectivity, speed and applicability in homogenization processes in very large climate data time series.

- According to [51] and [12], there are very few studies for homogenization of precipitation data, thus this issue should be a priority in homogenization research. This kind of data requires much great effort, as their variability is more spatially complex.

References

[1] http://www.ncdc.noaa.gov/ghcnm/v3.php (accessed February 9, 2016)

[2] https://crudata.uea.ac.uk/cru/data/temperature/#filfor (accessed February 9, 2016)

[3] http://www.meteo.noa.gr/ (accessed February 9, 2016)

[4] Steirou E.S., 2011. *Investigation and assessment of homogenization methods for hydroclimatic data.* NTUA, Athens.

[5] Cao L.J., Yan Z.W., 2012. Progress in research on homogenization of climate data. *Advances in climate change research*, **3(2)**, 59-67.

[6] Domonkos P., 2011a. Homogenizing time series: beliefs, dogmas and facts. *Adv. Sci. Res.* **6**, 167-172.

[7] Aguilar E., Auler I., Brunet M., Peterson T.C., Wieringa J., 2003. Guidelines on climate metadata and homogenization. *WMO/TD,* **1186**, *WCDMP*, **53**, World Meteorological Organization, Geneva.

[8] Peterson T.C., Easterling D.R., Karl T.R., Groisman P., Nicholls N., Plummer N., Torok S., Auler I., Boehm R., Gullett L., Vincent L., Heino R., Tuomenvirta H., Mestre O., Snentimrey T., Salinger J., Forland E., Hanssen-Bauer I., Alexandersson H., Jones P., Parker D., 1998. Homogeneity adjustments of in situ atmospheric climate data. *Int. J. Climatol.* **18**, 1493-1517.

[9] Guijarro J., 2011. Influence of networking density on homogenization performance. *Proceedings of the seventh Seminar for Homogenization and Quality Control in Climatological Databases* (eds. Lakatos M., Szentimrey T., Vincze E.). World Meteorogical Organization, Budapest, Hungary, WMO-TD, **1493**, 25-36.

[10] Reeves J., Chen J., Wang X.L., Lund R., Lu Q., 2007. A review and comparison of changepoint detection techniques for climate data. *J. Appl. Meteorol. Climatol,* **46(6),** 900-915.

[11] Lindau R., Venema V., 2013. On the multiple breakpoint problem and the number of significant breaks in homogenization of climate records. *Idojaras,* **117 (1),** 1-34.

[12] Ribero S., Caineta J., Costa A.C., 2015. Review and discussion of homogenization methods for climate data. *Physics and Chemistry of the Earth* (in press).

[13] Beaulieu C., Seidou O., Ouarda T.B.M.J., Zhang X., 2009. Intercomparison of homogenization techniques for precipitation data continued: comparison of two recent Bayesian change-point models. *Water Resour. Res.,* **45,** W08410.

[14] Domonkos P., 2011b. Efficiency evaluation for detecting inhomogeneities by objective homogenization methods. *Theor. Appl. Climatol.,* **105 (3-4),** 455-467.

[15] Von Neumann J., 1941. Distribution of the ratio of the mean square successive difference to the variance. *Ann. Math. Stat.,* **13,** 367-395.

[16] Wald A., Wolfowitz J., 1943. An exact test for randomness in the non-parametric case based on serial correlation. *Ann. Math. Stat.,* **14**, 378-388.

[17] Mann H., 1945. Non-parametric tests against trend. *Econometrica,* **13 (3)**, 245-259.

[18] Kendal M., 1975. *Rank Correlation Methods,* Charles Griffin, London.

[19] Wilcoxon F., 1945. Individual comparison by ranking methods. *Biometric Bull.,* **1,** 80-83.

[20] Mann H.B., Whitney D.R., 1947. On a test of whether one of two random variables is stochastically larger than the other. *Ann. Math. Stat.,* **18**, 50-60.

[21] Kruskal W., 1952. A non-parametric test for the several sample problem. *Ann. Math. Stat.,* **23**, 525-540.

[22] Kruskal W., Wallis W., 1952. Use of ranks in one-criterion variance analysis. *J. Am. Stat. Assoc.,* **47,** 583-621.

[23] Pettitt A.N., 1979. A non-parametric approach to the change-point detection. *Appl. Stat.,* **28 (2),** 126-135.

[24] Kohler M., 1949. Double-mass analysis for testing the consistency of records and for making adjustments. *Bull. Am. Meteorol. Soc.,* **30,** 188-189.

[25] Craddock J., 1979. Methods of comparing annual rainfall records for climatic purposes. *Weather,* **34**, 332-346.

[26] Potter K., 1981. Illustration of a new test for detecting a shift in mean in precipitation series. *Mon. Weather Rev,* **109,** 2040-2045.

[27] Buishand T., 1982. Some methods for testing the homogeneity of rainfall records. *J. Hydrol.,* **58,** 11-27.

[28] Easterling D.R., Peterson T.C., 1995. A new method for detecting and adjusting for undocumented discontinuities in climatological time series. *Int. J. Climatol.,* **15,** 369-377.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[29] Vincent L.A., 1998. A technique for the identification of inhomogeneities in Canadian temperature series. *J. Climate*, **11,** 1094-1104.
[30] Allen R., Pereira L., Raes D., Smith M., 1998. Statistical Analysis of Weather Data Sets, Crop Evaporation – Guidelines for Computing Crop Water Requirements, FAO- Food and Agriculture Organization of the United Nations (Eds.). *FAO Irrigation and Drainage Paper 56, Annex IV*, Rome.
[31] Seidou O., Ouarda T.B.M.J., 2007. Recursion-based multiple changepoint detection in multiple linear regression and application to river streamflows. *Water Resour. Res.,* **43**, W07404.
[32] Seidou O., Asselin J.J., Ouarda T.B.M.J., 2007. Bayesian multivariate lineal regression with application to changepoint models in hydrometeorological variables. *Water Resour. Res.*, **43,** W08401.
[33] Ruggieri E., 2013. A Bayiesian approach to detecting change points in climatic records. *Int. J. Climatol.,* **33 (2),** 520-528.
[34] Hannart A., Naveau P., 2009. Bayesian multiple change points and segmentation: application to homogenization of climatic series. *Water Resour. R.*, **45 (10),** W10444.
[35] Gallagher C., Lund R., Robbins M., 2012. Changepoint detection in daily precipitation data. *Environmetrics,* **23 (5),** 407-419.
[36] Beaulieu C., Ouarda T.B.M.J., Seidou O., 2010. A Bayesian normal homogeneity test for the detection of artificial discontinuities in climatic series. *Int. J. Climatol.*, **30 (15),** 2342-2357.
[37] Alexandersson H., 1986. A homogeneity test applied to precipitation data. *J. Climatol.,* **6,** 661-675.
[38] Alexandersson H., Moberg A., 1997. Homogenization of Swedish temperature data. Part I: Homogeneity test for linear trends. *Int. J. Climatol.,* **17 (1),** 25-34.
[39] Szentimrey T., 1999. Multiple analysis of series for homogenization (MASH). *Proceedings of the Second Seminar for Homogenization of Surface Climatological Data,* Budapest, Hungary, WMO, WCDMP, **41,** WMO-TD 1962, 27-46.
[40] Caussinus H., Mestre O., 1996. New mathematical tools and methodologies for relative homogeneity testing. *Hungarian Meteorogical Service, Proceedings of the First Seminar for Homogenization of Surface Climatological Data*, Budapest, Hungary, 63-82.
[41] Caussinus H., Mestre O., 2004. Detection and correction of artificial shifts in climate series. *J. R. Stat. Soc. Ser. C. Appl. Stat.,* **53 (3),** 405-425.
[42] Costa A.C., Negreiros J., Soares A., 2008. Identification of inhomogeneities in precipitation time series using stochastic simulation. *GeoENV VI - Geostatstics for Environmental Applications* (eds. Soares A. Pereira M.J., Dimitrakopoulos R.), Springer, Netherlands, 275-282.
[43] Domonkos P., 2011c. Adapted Caussinus-Mestre algorithm for networks of temperature series (ACMANT). *Int, J. Geosci.,* **2 (03),** 293-309.
[44] Domonkos P., 2014. Homogenization of precipitation time series with ACMANT. *Theor. Appl. Climatol.*
[45] Guijarro J., 2006. Homogenization of a dense thermo-pluviometric monthly database in the Balearic Islands using the free contributed R package "Climatol". *Proceedings of the fifth Seminar for Homogenization and Quality Control in Climatological Databases* (eds. Lakatos M., Szentimrey T., Bihari Z., Szalai S.), World Meteorological Organization, Budapest, Hungary, WMO-TD, **1493,** 25-36.
[46] Wang X. L., 2008. Accounting for autocorrelation in detecting mean shifts in climate data series using the penalized maximal t or F test. *J. Appl. Meteorol. Climatol.,* **47 (9),** 2423-2444.
[47] Stepanek P., 2008a. *AnClim-Software for Time Series Analysis.* Dept. of Geography, Fac. Of Natural Sciences, MU, Brno.
[48] Stepanek P., 2008b. *ProClimDB-Software for Processing Climatological Datasets*. CHMI, Regional Office Brno.
[49] Menne M.J., Williams C.N., 2009. Homogenization of temperature series via pairwise comparisons. *J. Climate.* **22 (7),** 1700-1717.
[50] Mestre O., Domonkos P., Picard F., Auler I., Robins S., Lebarbier E., Bohm R., Aguilar E., Guijarro J., Vertachnik G., Klancar M., Dubuisson B., Stepanek P., 2013. HOMER: a homogenization software-methods and applications. *Idojaras,* **117(1),** 47-67.
[51] Auler I., Bohm R., Jurkovic A., Orlik A., Potzmann R., Schoner W., Ugersbock M., Brunetti M., Nanni T., Maugeri M., Briffa K., Jones P., Efthymiadis D., Mestre O., Moisselin J.M., Begert M., Brazdil R., Bochnicek O., Cegnar T., Gajic-Capka M., Zaninovic K., Majstorovic Z., Szalai S., Szentimrey T., Mercalli L., 2005. A new instrumental precipitation dataset for the greater alpine region for the period 1800-2002. *Int. J. Climatol.,* **25 (2),** 139-166.

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QGIS plugin development for automating a pressures-impacts analysis method, in the context of the European Water Framework Directive 2000/60

E. Kourliti[1], Z. Mallios[1,2*], N. Theodossiou[1,2]

[1] Interdisciplinary Postgraduate Program "Ecological quality and water management at a river basin level", Departments of Biology, Geology and Civil Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece
[2] Division of Hydraulics and Environmental Engineering, Department of Civil Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece.
*Corresponding author: Email: zmallios@civil.auth.gr

Abstract

The aim of the present study was the development of a plugin tool in Quantum Geographical Information System - QGIS 2.10.1 Pisa, for pressures – impacts analysis, according to the specifications of the European Water Framework Directive 2000/60 (WFD) and the recommendations of the WFD Common Implementation Strategy IMPRESS Working Group. The methodology that was automated, was first applied in Gallikos River basin during a case study about its ecological status that was carried out in the context of the Interdisciplinary Postgraduate Program of Studies *Ecological quality and water management at a River basin level*. The data on which the tool was developed come also from the aforementioned study, in which *in situ* data are also included (biological, physico-chemical and hydromorphological elements) from 14 field samples along the Gallikos River (May 2013). The tool calculates pollution pressures and pressures from morphological alterations, estimates the significant ones by comparing them to thresholds, coming from legislation and literature, and assesses impacts and risk of not achieving WFD environmental objectives per surface water body applied each time.

The tool was developed using the QGIS Plugin Builder, while the graphical user interface (GUI) was designed in Qt Designer (with QGIS 2.10.1 Custom Widgets) and the related functions were programmed using Python 2.7 programming language and the PyQt bindings (Qt4). The tool is accessed through a button on the main QGIS Menu and a user friendly GUI. Data on which it can be applied must be of a certain format and should refer to one surface water body each time. Addition of new fields and attributes in the attribute tables of shapefiles, area and length calculations, application of spatial analysis method (intersect), selection by attributes, addition of new shapefiles and drawing of new layers on the QGIS canvas and exporting results in text file (.txt) are the basic functions on which the tool was developed. The tool is useful during the pressures – impacts analysis as, it achieves automation of the relative computational, logical and cartographical processes and produces accurate results in a short time, thus reducing the human and time effort as well as the chances of error when applying the methodology.

Keywords: QGIS; Plugin; Pressures – Impacts analysis (IMPRESS); Water Framework Directive.

1. INTRODUCTION

The objective of pressures – impacts analysis, which is required under Article 5 of the European Water Framework Directive 2000/60 (WFD), is the risk assessment per water body of not achieving the environmental objectives that the WFD sets for each water category. According to Guidance Document No 3, produced by the Common Implementation Strategy IMPRESS Working Group 2.1 - Analysis of Pressures and Impacts [1] - the key components in the analysis of pressures and impacts are to (i) identify driving forces and pressures, (ii) identify potentially significant pressures,

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(iii) assess the impacts along with monitoring data and (iv) evaluate the likelihood of failing to meet WFD objectives. The results of the pressures - impacts analysis are crucial when designing monitoring programs and developing and selecting the appropriate measures. Pressures can come from point and nonpoint sources of pollution, morphological alterations, and hydromorphological modifications or can be other types of pressures. A pressure can be significant if, on its own or in combination with other pressures, contributes to an impact that may result in the failing of a WFD objective. As stated in the GD No 3 "this requires an understanding of the nature of the impact that may result from a pressure, and appropriate methods to monitor or assess the relationship between impact and pressure". Furthermore, the results of the pressures – impacts analysis should clearly and transparently help differentiate and prioritize measures to be applied for these water bodies failing to meet the WFD objectives. For that it is important that pressures are allocated to their sources and therefore to the responsible sectors (e.g. agricultural, industrial, urban activity), so that measures can later be designed based on the required reductions of the pressures intensity to such levels that permit the achievement of WFD environmental objectives [2].

Pressures - impacts analysis constitutes a multistep process, requiring management and synthesis of many data coming from different sources. The purpose of this study was to develop a plugin tool in a Free and Open Source Software (FOSS) Geographic Information System (GIS), the Quantum GIS (QGIS), in order to be applied in the pressure – impacts analysis, under the WFD requirements and the recommendations by the IMPRESS Working Group. QGIS was chosen as it is free to download, easy to set up and use, while at the same time it is strongly supported by on line material and help. QGIS is published under GNU General Public License (GPL) and is considered as one of the mature FOSS [3,4]. QGIS functionality can be extended through python console, Script Runner, Graphical Modeler or plugin development, by accessing the QGIS Python (PyQGIS) Application Program Interface (API) [5,6]. Through PyQGIS API, which is based on QGIS C++ API, every aspect of QGIS can be controlled. PyQGIS API is not often updated, but it is identical to C++ API, which is very well documented [7].

More specific the tool presented in this paper, was developed in order to automate the methodology applied during a case study in Gallikos River basin, about its ecological status which was carried out in the context of the Interdisciplinary Postgraduate Program of Studies of the Aristotle University of Thessaloniki "Ecological quality and water management at a River basin level". The data on which the tool was developed come also from the aforementioned study, in which in situ data are also included (biological, physico-chemical and hydromorphological elements) from 14 field samples along the Gallikos River (May 2013). Specific objectives were: (i) organize the data, (ii) automate the computational, logical and cartographical processes, (iii) design a user-friendly interface for the plugin tool, (iv) reduce time and human effort needed during pressures – impacts analysis and (v) produce accurate results, reducing the chances of error.

2. MATERIALS AND METHODS

2.1 Methodology

The methodology, that was automated, requires calculations of pollution pressures (BOD_5, TN, TP, and TSS from urban, livestock and land uses) using immission factors coming from the literature [8,9,10] and calculation of pressures from morphological alterations using the proportion of different land uses in the study area (agriculture areas, length of the river running through agriculture areas, urban areas). Then, follows the estimation of the significant pressures, by comparing the magnitude of pollution pressures to thresholds set by the legislation [11,12], and to thresholds set by the literature, for the morphological pressures [13,14]. Finally, the assessment of the impacts and the risk of not achieving WFD environmental objectives per surface water body is done according to the Spanish WFD water pressures-impacts analysis method [9,15].

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The tool was developed as a plugin for QGIS 2.10.1 Pisa, using QGIS Plugin Builder. The Graphical User Interface (GUI) was designed in Qt Designer (with QGIS 2.10.1 Custom Widgets) and the related functions were programmed using Python 2.7 programming language and the PyQt bindings (Qt4). Pretty table 0.7.2, a Python library by Luke Maurits, was used in order to export the results to a text file in a readable format [16].

2.2 Data

The tool implements pressures-impacts analysis per sub basin of a water body, so that pressures can afterwards be attributed to the water body. For that, and in order for someone to use the plugin tool, apart from that all required data should be stored in shapefiles and have the same Coordinate Reference System, all shapefiles should, at the same time, have the same geographical extension of the polygon shapefile that represents the sub basin of the water body, for which the analysis will be applied (Figure 1). The required shapefiles should hold the following information (Figure 2): (i) the settlements of the area, as points, along with the residents population and the type of urban wastewater management type per settlement, (ii) the settlements, as points, along with the livestock population per animal category and per settlement, (iii) the land uses, as polygons, according to the 3rd level coded of the Corine Land Cover 2000 program, (iv) the hydrographic network, i.e. the water body, as line, (v) the polygon shapefile representing the sub basin and optionally (vi) the sampling sites, as points, along with the monitoring data per settlement.

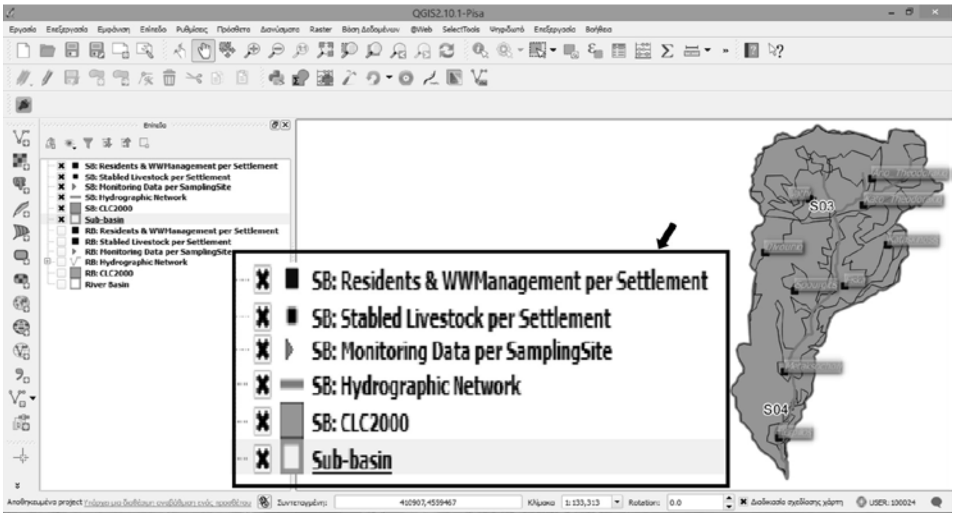


Figure 1. Required shapefiles

Residents & urban wastewater treatment

POINT_X	POINT_Y	Settlement	Pop	WWManagType
411358.787	4552764.79	Divounio	46	2
412078.262	4543387.64	Terpillos	483	2
412370.482	4546718.1	Metaksochori	68	2
412887.907	4550840.84	Spourgitis	50	2
413617.966	4555464	Vathi	309	2
415411.9	4551072.15	Fiska	152	2
416390.351	4555176.3	Kato_Theod	97	2
416813.665	4556513.84	Ano_Theod	53	2
417590.979	4553142.92	Kataskinosis	0	2

Land uses

ID	AREA	PERIMETER	CLC_CODE
731	648500.324	3241.30097	243
760	26546.5138	699.245783	311
763	263452.053	2225.53946	243
764	19987.8792	599.844443	324
789	45410.8983	1015.05494	324
794	510176.461	3710.84971	243
800	362327.953	2877.24118	311
806	126366.67	1656.33604	324
820	4306047.82	14379.9628	243
856	1029983.32	5630.06392	243

Stabled livestock

POINT_X	POINT_Y	Settlement	Horses	Bovines	Bovines_fe	Pigs	Sheep	Poultry
411358.787	4552764.79	Divounio	0	7	35	27	510	560
412078.262	4543387.64	Terpillos	2	223	257	306	5018	4605
412370.482	4546718.1	Metaksochori	0	0	0	0	0	0
412887.907	4550840.84	Spourgitis	0	0	0	0	0	0
413617.966	4555464	Vathi	9	48	63	65	4184	630
415411.9	4551072.15	Fiska	9	50	242	22	2459	1980
416390.351	4555176.3	Kato_Theod	0	20	20	28	716	738
416813.665	4556513.84	Ano_Theod	0	0	0	0	0	0
417590.979	4553142.92	Kataskinosis	0	0	0	0	0	0

Monitoring data

Site_ID	POINT_X	POINT_Y	T_Air	T_Wat	pH	BOD	DO	TSS	Cond	NO3	NO2
S04	412633.2015	4544488.15	33.1	19.2	8.08	6	10.9	6.4	0.72	0.828678	0.031439
S03	414969.4965	4554783.06	30.7	17	6.8	3.2	9.2	30.2	0.615	0.905495	0.013638

Site_ID	POINT_X	POINT_Y	NH4	PO4	Discharge	RM	WB	STAR	HESY	QBR	HMS	IHF
S04	412633.2015	4544488.156	0.08	0.012	0.06	RM1	N	0.41	2	65	2	70
S03	414969.4965	4554783.064	0.02	0.02	0	RM1	N	0.65	3	90	2	64

Figure 2. Required data

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3. RESULTS AND DISCUSSION

The tool is accessed through a button on the main QGIS Menu and a Graphical User Interface (GUI), which consists of three parts: Study Area, Pressures and Quality elements (Figure 3). The last part can be activated or deactivated, depending on the availability of monitoring data or not. If there are not available monitoring data, then the tool can implement only pressures analysis (calculation of pressures and estimation of the significant ones). If there are available monitoring data, then the tool implements also impacts analysis, thus estimating the risk for the water body not to achieve the WFD environmental objectives. In each part of the GUI, the user must select the appropriate shapefile and the fields of the corresponding attribute table that are being available once the shapefile is selected. Mean daily discharge field can be filled only if the Quality elements part is activated and this value is used in order to adjust the threshold values, for the significant pollution pressures, to the sub basin.

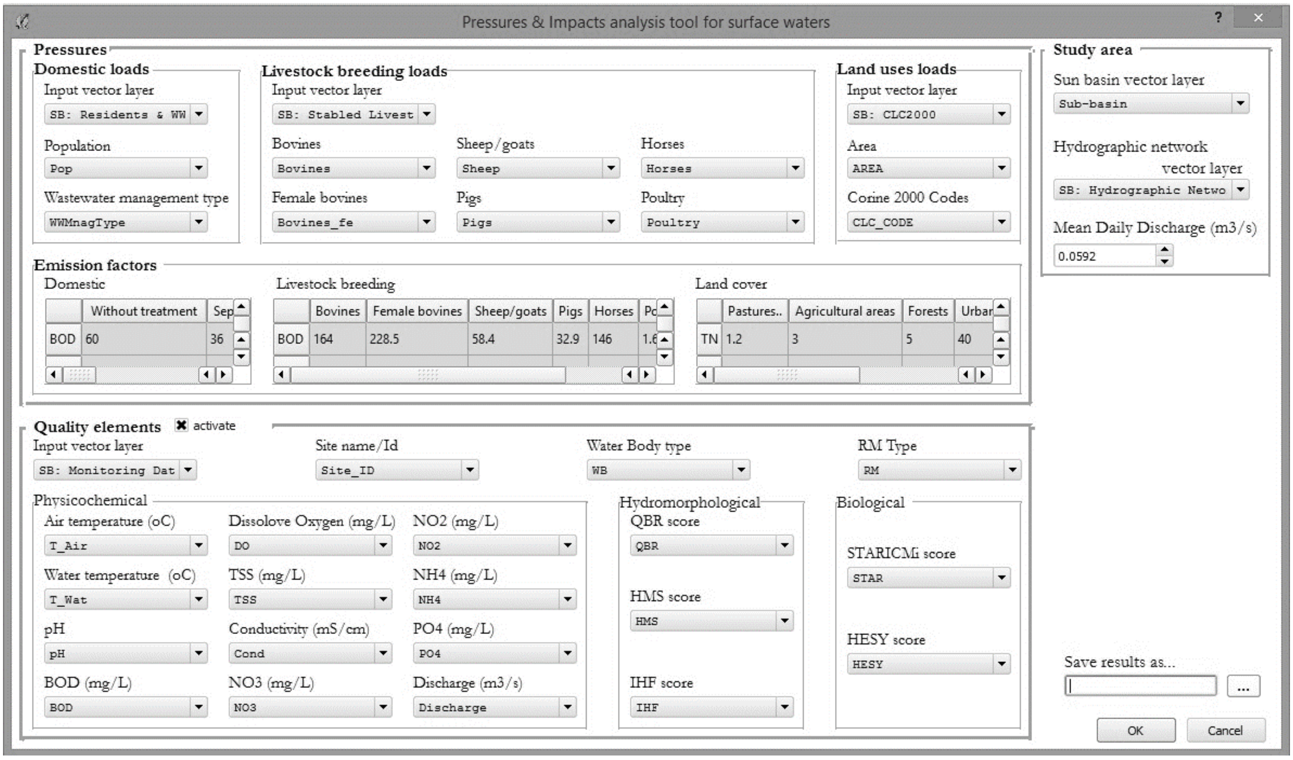


Figure 3. Graphical User Interface

Results are produced as new descriptive information added to the shapefiles attribute tables, as new layers added to the QGIS canvas (Table 1) and as a report in the form of a text file (.txt) (Table 1). A new shapefile is produced and added to the QGIS canvas, after the application of spatial analysis method Intersect for the shapefiles of land uses and the hydrographic network, in order to calculate the proportion of the river through the different land uses.

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Table 1. Required data and results

Pressures	Data	Results	
	Attribute table	Attribute table	New layer
Urban Waste water	Residents population	Pop_Class	√
	Urban waste water management type		√
		BODkgy, TNkgy, TPkgy, TSSkgy BODkgd, TNkgd, TPkgd, TSSkgd	
Stabled livestock	Bovines population	BODbov, TNbov, TPbov, TSSbov	
	Female bovines population	BODfbov, TNfbov, TPfbov, TSSfbov	
	Sheep population	BODsh, TNsh, TPsh, TSSsh	
	Pigs population	BODpig, TNpig, TPpig, TSSpig	
	Horses population	BODhors, TNhors, TPhors , TSShors	
	Poultry population	BODpoul, TNpoul, TPpoul, TSSpoul	
		BODkgy, TNkgy, TPkgy, TSSkgy BODkgd, TNkgd, TPkgd, TSSkgd	
Land uses	3rd level Corine Land Cover codes	Areaha, Alevel, Gen_Categ, Specific, Sel_Categ TNkgy, TPkgy TNkgd, TPkgd	√ √
Monitoring data	Indices QBR[17], HMS[18], IHF[19] STAR[20], HESY[21]	QBRexpl, HMSexpl, IHFexpl STARexpl, HESYexpl	√ √

As shown in Figure 4, the text file consists of two parts. The first part, which can only be read but not inserted in a proper way in other software, and the second part, which consists of the same results but in such a format that permits their insertion in other software (with «?» as delimiter).

```
------------------------------R E S U L T S--------------------------------------------------------------------------------
Part A
>>PRESSURES FROM POINT & NON POIN SOURCES OF POLLUTION - RIVER BASIN
Table_a: Stabled livestock emissions loads in the sub-basin
Table_b: Land uses: Area & Immissions loads for selected categories of land uses in the sub-basin
Table_c: Emissions loads (kg/d) in the sub-basin from all point sources of pollution
Table_d: Immissions loads (kg/d) in the River basin from all point sources of pollution
Table_e: Participation rate of each point source of pollution in a pollutant's total immissions loads (kg/d)
Table_f: Permitted levels of pollutant loads (kg/m3)
Table_g: Total permitted levels of Total N, Total P, BOD and TSS for the River basin
------- Significant pressures from point & non-point sources of pollution
>>PRESSURES FROM MORPHOLOGICAL ALTERATIONS - RIVER BASIN
Table_h: Land uses in the sub basin (general categories)
Table_i: River length through the different sub-basin land uses (general categories)
------- Significant pressures from morphological alterations
>>MONITORING DATA: BIOLOGICAL, PHYSICOCHEMICAL & HYDROMORPHOLOGICAL ELEMENTS
Table_j: Min, max, mean and range values for Physico-chemical parameters
Table_k: Sampling sites exceeding permitted limits for fish life and drinking water
Table_l: QBR, RHS–HMS, IHF indices per River sampling site
Table_m: Water quality assessment according to HESY and STAR_ICMi indices per River sampling site
Part B
-------.txt file with delimiter "?" -------
Example:
Female bovines?917.72?21.99?134.14?13.24?2554.19?23.81?17136.0?77.09
Sheep/goat?2857.61?68.48?820.01?80.92?7255.84?67.65?0.0?0.0
Pigs?35.62?0.85?11.22?1.11?160.53?1.5?121.01?0.54
Horses?18.54?0.44?3.19?0.31?28.4?0.26?0.0?0.0
Poultry?169.99?4.07?0.0?0.0?76.02?0.71?198.32?0.89
Domestic?317.83?109.69?59.43?
Livestock?2145.03?625.97?30.4?22228.45
```

Figure 4. Results in the text file

4. CONCLUSIONS

QGIS proved easy to install, user-friendly, while at the same time it provides different and powerful ways to extend its functionalities. Both directly from the menu and through the development and use of plugins, QGIS provides all those features that are necessary for the management, processing, and visualization of the data required in the methodology which was automated. The plugin tool developed and presented in this paper, is useful during the pressures – impacts analysis as, it achieves automation of the relative computational, logical and cartographical processes and produces accurate results in a short time, thus reducing the human and time effort as well as the chances of error when applying the methodology. The tool calculates pollution pressures and pressures from morphological alterations, estimates the significant ones by comparing them to

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thresholds set by the literature and legislation, and assesses impacts and risk of not achieving WFD environmental objectives per surface water body according to the Spanish WFD water pressures - impacts analysis method.

In its current version, the tool can be used:

- For the pressures-impacts analysis methodology for which was developed and the production of results in the following ways: as new descriptive information added to the shapefiles attribute tables, as new shapefile and layers added to the QGIS canvas and as a report in the form of a text file (.txt).
- For the pressures-impacts analysis at a sub-basin level (i.e. per surface water body), so that pressures can afterwards be attributed to the water body.
- With or without monitoring data, activating or deactivating the corresponding part of the GUI.

It should be noted that with the current version of the tool, not all possible pollution pressures are under consideration (e.g. industrial, mining activities, aquacultures etc.). Therefore, the inclusion of more criteria concerning pressures and the development of the tool to run independently of the sub basins number (and not for one sub basin at a time), are some of the coming improvements, along with the code optimization and the GUI improvement after users evaluations. Finally, more spatial analysis methods could be included (e.g. zone buffering, DRASTIC model for underground water bodies, spatial interpolation methods in order to estimate parameters where no monitoring data is available etc.), making the tool more powerful in the pressures – impacts analysis.

References

[1] WFD Common Implementation Strategy Working group 2.1: IMPRESS, 2003. Guidance on the Analysis of Pressures and Impacts. Office for Official Publications of the European Communities.

[2] European Commission, 2015. Staff Working Document – Report on the progress in implementation of the Water Framework Directive Programmes of Measures, accompanying the Communication 'The Water Framework Directive and the Floods Directive: Actions towards the 'good status' of EU water and to reduce flood risks'. SWD (9.3.2015), 50 final.

[3] Steiniger S., Hunter A.J.S., 2013. The 2012 free and open source GIS software map – A guide to facilitate research, development, and adoption. *Computers, Environment and Urban Systems*, **39**: 136–150.

[4] Chen D., Shams S., Carmona-Moreno C., Leone A., 2010. Assessment of open source GIS software for water resources management in developing countries. *Journal of Hydronviron- ment Research*, **4**(**3**): 253–264.

[5] Lawhead, 2015. *QGIS Python Programming Cookbook*. Packt Publishing Ltd, Birmingham, UK.

[6] Menke, Smith, Pirelli & Hoesen, 2015. *Mastering QGIS*. Packt Publishing Ltd, Birmingham, UK.

[7] http://qgis.osgeo.org (accessed February 28th, 2016)

[8] Andreadakis A., Gavalakis E., Kaliakatsos L., Noutsopoulos C., Tzimas A., 2007. The implementation of the Water Framework Directive (WFD) at the river basin of Anthemountas with emphasis on the pressures and impacts analysis, Ninth Environmental Science and Technology Symposium, September 1–3, 2005, Rhodes, Greece. *Desalination*, **210**(**1-3**): 1-15.

[9] Ioannou A., Chatzinikolaou Y., Lazaridou M., 2009. A preliminary pressure–impact analysis applied in the Pinios River Basin (Thessaly, Central Greece). *Water and Environment Journal*, **23**(**3**): 200-209.

[10] Economopoulos, 1993. *Assessment of sources of air, water and land pollution. Guide to rapid source inventory techniques and their use in formulating environmental control strategies. Part one: Rapid inventory techniques in environmental pollution*. World Health Organization, Geneva.

[11] European Commission, 2006. Directive 2006/44/EC of the European Parliament and of the Council of 6 September 2006 on the quality of fresh waters needing protection or improvement in order to support fish life (L 264/20)

[12] Greek Joint Ministry Decision 2600/2001, 2001. Drinking water quality in accordance to the European Directive 98/83.

[13] LAWA, 2003. Working Group Water of the Länder, German Guidance Document for the implementation of the EC Water Framework Directive. Länderarbeitsgemeinschaft Wasser, Mainz, Germany

[14] UK Environment Agency, 2005. Technical assessment method: Morphology in rivers and identification of provisional Artificial/Heavily Modified Water Bodies. Unpublished Report, Water Framework Directive Programme, Environment Agency.

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C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
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[15] Castro, Infante, Rodriguez, Lerma, & Martínez, 2005. Manual para la identificacion de las presiones y análisis del impacto en aguas superficiales. Centro de Publicaciones, Ministerio de Medio Ambiente–Dirección General del Agua, Madrid, Spain.
[16] https://pypi.python.org/pypi/PrettyTable (accessed February 28th, 2016)
[17] Munné A., Prat N, Solà C., Rieradevall M. 2003. A simple field method for assessing the ecological quality of riparian habitat in rivers and streams: QBR index. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **13**(**2**): 147–163.
[18] Raven P., Boon P., Dawson F., Ferguson A., 1998. Towards an integrated approach to classifying and evaluating rivers in the UK. *Aquatic conservation: Marine and Freshwater Ecosystems*, **8**(**4**): 383-393.
[19] Pardo I., Álvarez M., Casas J.J., Moreno J.L., Vivas S., Bonada N., Alba-Tercedor J., Jáime P., Moyá G., Prat N., Robles S., Suárez M.L., Toro M., Vidal-Abarca M.R., 2002. El hábitat de los ríos mediterráneos. Diseño de un índice de diversidad de hábitat. *Limnetica*, **21**(**3-4**): 115-133.
[20] Buffagni A., Erba S., Cazzola M., Murray-Bligh J., Soszka H., Genoni P., 2006. The STAR common metrics approach to the WFD intercalibration process: Full application for small, lowland rivers in three European countries. *Hydrobiologia*, **566**: 379–399.
[21] Artemiadou V., Lazaridou M. 2005. Evaluation score and interpretation index for the ecological quality of running waters in central and Northern Hellas. *Environmental Monitoring and Assessment*, **110**: 1-40.

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XIII

Study of organic fluorine pollutants in human serum, hair and nails to explore ideal bioindicators

H. Zhang[1*], D. Yao[1], R. Zhang[1,2], S. Yin[1], Z. Chai[3], J. Shen[4], B. Yang[5]

[1] College of Physics and Energy, Shenzhen University, Shenzhen 518060, China
[2] Brandeis University, Waltham 02453, MA, U.S.A
[3] Multidisciplinary Initiative Center, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
[4] Inspection Center of Import and Export Food, Shenzhen Entry–Exit Inspection and Quarantine Bureau of PRC, Shenzhen 518045, China
[5] College of Chemistry and Environment, Shenzhen University, Shenzhen 518060, China
*Corresponding author: Email: zhangh@szu.edu.cn

Abstract

To explore better bioindicators of perfluoroalkyl acids (PFAAs) for health risk assessment, the contents of total fluorine (TF), extractable organic fluorine (EOF) and 15 target PFAAs in human serum (n=60), hair (n=49) and nails (n=39) from Guangdong, China, were measured using cyclic neutron activation analysis (CNAA) combined with high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). This hybrid method provides both bulk contents of TF，EOF and concentrations of target PFAAs species in samples. The results indicated that EOF was the major form of fluorine in serum, accounting for 70 %-80 % of TF, but the minor form in hair and nails, accounting for 11 %-41 %. In serum, hair and nails, the level of identified fluorine, which is the concentration of all target PFAAs expressed as elemental fluorine, each contributed less than one third of EOF. The contents of ∑PFAAs and EOF in the three matrices were in the orders of nail ≈ hair >> serum and nail >> hair >> serum, respectively. Significant positive correlations were observed between nails and serum for the three major PFAAs species, including Perfluorooctane sulfonate (PFOS, $p<0.01$), perfluorooctanoic acid (PFOA, $p<0.05$) and perfluorohexane sulfonate (PFHxS, $p<0.01$), suggesting that human nails, a non-invasive sample, is a promising bioindicator for PFAAs risk assessment.

Keywords: bioindicator; perfluoroalkyl acids (PFAAs); perfluorooctane sulfonate (PFOS); perfluorooctanoic acid (PFOA); human serum; hair and nails

1. INTRODUCTION

Perfluoroalkyl acids (PFAAs), though widely applied in industrial and daily products as outstanding surfactants, accumulate in biosphere and cause mitochondrial disorder, fat metabolic disturbance, as well as intoxications in reproduction and nervous system, etc [1]. Furthermore, considering that perfluorooctane sulfonate (PFOS) and its sulfonate derivative possess strong environmental persistence, high bioaccumulation, toxicity and capability to transmit in long range, the Stockholm Convention added 9 new persistent organic pollutants (POPs) including PFOS and its sulfonate, perfluorooctane sulfonyl fluoride, into the latest blacklist on August 26th, 2010 [2]. This attracted high attention to the health risk evaluation of PFAAs in human body, which requires suitable biological samples.

Absorbed PFAAs mainly bind with serum proteins [3] and stay in serum, which usually indicates the PFAAs exposure risk in human body. However, blood collection has various

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deficiencies, including injuries, legal restrictions, high cost, inconvenient storage, etc. In contrast, hair and nails are easy for collection and storage, which prevents the possibility of infection caused by invasive sampling. Their collections are not restricted by age, gender, or regions, etc. More importantly, through the abundant capillaries in hair follicles and nail beds, PFAAs can enter and deposit in hair and nails. Hair and nails consist of keratin, which is resistant against acid, alkali and enzymatic degradations, thus can record the historical levels of chemicals in body [4]. Therefore, to determine the feasibility of evaluating human PFAAs exposure through hair and nails, it is particularly necessary to compare the PFAAs residues in serum with those in hair and nails.

Currently, high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) is the most effective way to analyze PFAAs. However, most PFAAs have no standard substances and cannot be analyzed by chromatographic analysis. Therefore, PFAAs analysis should be combined with total fluorine (TF) and extractable organofluorine (EOF) bulk analysis to reduce its dependency on standard substances and reflect the PFAAs residues in samples more objectively.

Cyclic neutron activation analysis (CNAA) is a non-invasive nuclear method for TF measurement with small matrix effect. Therefore, it requires no pretreatment and possesses strong traceability. Besides, CNAA is especially appropriate for analyzing short-lived nuclides ($t_{1/2}$<60s) including ^{20}F($t_{1/2}$ =11.03 s), because it increases the signal-noise ratio (SNR) and counting rate of short-lived nuclides significantly by periodically repeating the procedure of traditional neutron activation analysis (irradiation → cooling → counting). Because of the stable and high neutron flux (10^{10}-10^{12} $n \cdot cm^{-2} \cdot s^{-1}$) supplied by miniature neutron source reactor (MNSR), as well as the features of ^{20}F from the nuclear reaction $^{19}F(n, \gamma)\,^{20}F$, it is convenient for CNAA to quantitatively analyze trace TF and EOF in samples.

We combined HPLC-MS/MS and CNAA to determine the concentrations of TF, EOF, identified fluorine (IF, total concentration of identified PFAAs quantified as fluorine) and PFAAs in human serum, hair and nails. The correlations and significant differences between TF, EOF, IF and PFAAs in different matrices and sample groups were also analyzed. This study aimed to evaluate the potential of hair or nails as more appropriate biological samples for reflecting human exposure levels of new POPs.

2. MATERIALS AND METHODS

2.1 Sampling and pretreatment

Samples of serum (n=60), hair (n=49, including 10 permed or dyed hair) and nails (n=39) were obtained from volunteers age 19-26 in Shenzhen University during June and August, 2009.

Blood samples of about 10mL were collected from each volunteer using venipuncture into clean polypropylene (PP) tubes that were pre-rinsed with methanol. Serum was separated from blood by centrifugation at 4000 rpm for 15 min after coagulation. Supernatant was transferred to another clean PP tube, and stored at -20℃. Further pretreatment for serum is outlined in Fig. 1.

Nails and hair samples were separately placed into 15mL and 50mL PP tubes and washed twice with 1% aqueous solution of Triton-100 in an ultrasonic bath for 20 min, rinsed three times with ultrapure water and once with acetone to remove exogenous contamination, then dried at room temperature. The washed nails and hair samples were cut into pieces of about 3mm and wrapped in foil. Further pretreatment for nails and hair is outlined in Fig. 2.

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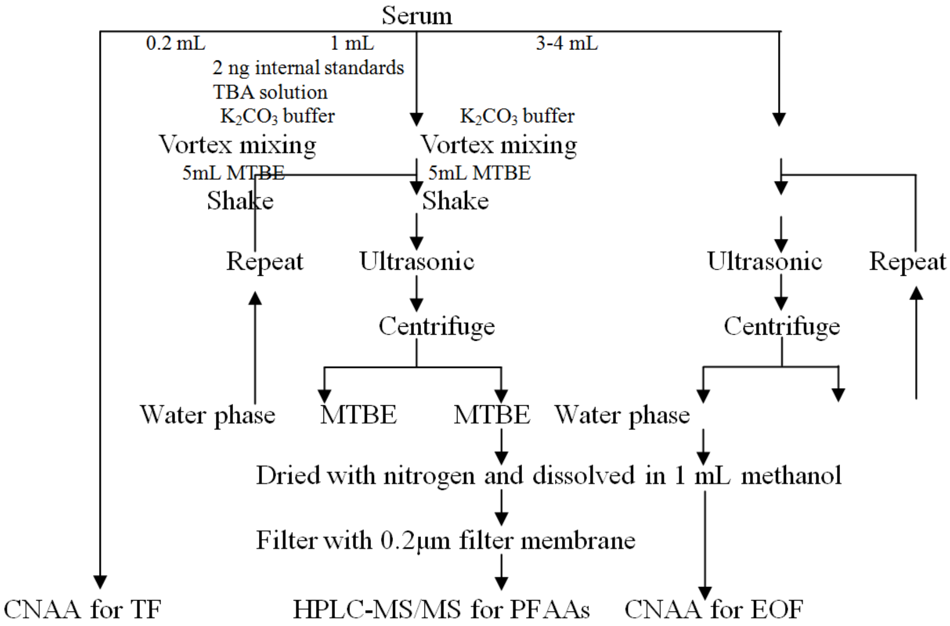


Figure 1: Procedure of serum pretreatment

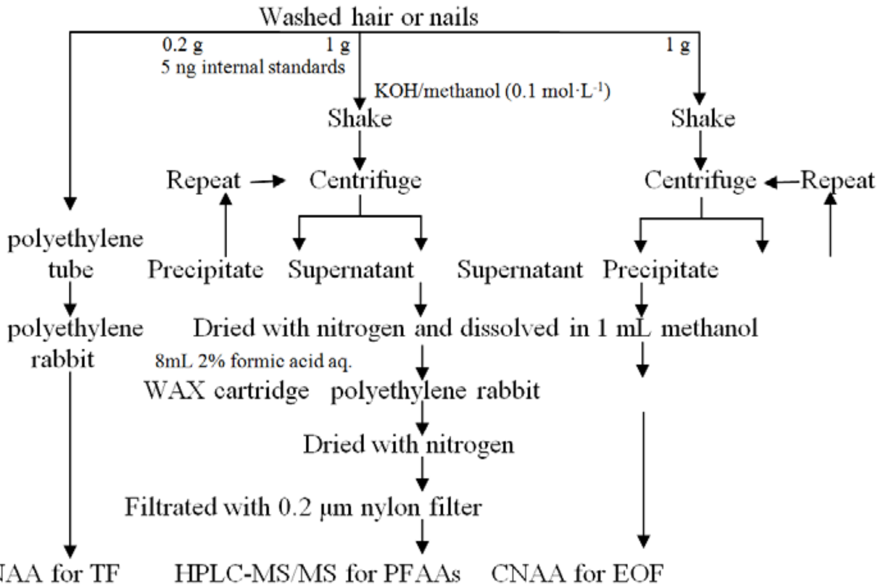


Figure 2: Procedure of hair and nails pretreatment

2.2 Analysis

TF and EOF in serum, nails and hair were determined by CNAA on a MNSR at Shenzhen University, under a neutron flux of $9\times10^{11}cm^{-2}\cdot s^{-1}$ and the conditions of irradiation time (t_i) = counting time (t_c) = 30 s, delay time (t_d) = waiting time (t_w, time between the end of counting and the start of irradiation) = 2 s, for 7 cycles. 0.2 mL serum, 0.2 g hair or 0.2 g nails was used for TF determination (Fig. 1&2). Serum was heat-sealed into a 1.5 mL centrifuge tube, then into a capsule. Hair and nails were heat-sealed into a polypropylene bag (1.5×1.5 cm^2), then into a capsule. 1.0 mL aliquots of extracts of serum, hair and nails were taken respectively for EOF determination. The extract was heat-sealed into a 1.5 mL centrifuge tube, then into a capsule (Fig. 1&2). The capsules

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were separately irradiated in the inner channel of the MNSR for CNAA. The signal of ^{20}F ($t_{1/2}$=11s, E_γ=1633 KeV) from $^{19}F(n, \gamma)^{20}F$ was measured by a high pure germanium coaxial detector (18% relative efficiency, ORTEC) coupled with a high throughput digital spectrometer (DSPEC Plus multichannel analyzer, ORTEC). Relative method was used for quantification and the interference coefficient of 0.012 [5] was used to subtract the interference of Na to F from $^{24}Na(n, \alpha)^{20}F$. The limits of detection (LOD) for TF in serum, hair and nails were 0.58 μg, 0.61 μg and 0.60 μg, respectively, while the LOD for EOF in the three matrices was 0.20μg.

PFAAs in serum, nails and hair were determined on a tandem mass spectrometer (API 3000, Applied Biosystems, Foster City, USA) connected to an high performance liquid chromatography (Agilent HP1100). A 20μL aliquot of extract was injected into a XDB C18 column (2.1mm×150mm×3.5μm, Agilent, USA) with column temperature of 50 °C and flow rate of 0.3 mL/min. The mobile phase consisted of methanol (A) and 2 mmol·L^{-1} ammonium acetate (B). The triple-quadruple mass spectrometer was operated in the negative electrospray (ESI) mode with multiple-reaction-monitoring (MRM). The gradient elution program and mass spectrometric parameters of target compounds are same as another study [6].

2.3 Quality Assurance and Control

For CNAA, centrifuge tubes, polyethylene bags and capsules were pre-rinsed with HNO_3 and H_2O. Their blanks were carefully checked and no signal was observed at 1633 KeV. The interference of Na to F was subtracted from all results. For PFAAs, all vessels were pre-rinsed with methanol and analyses were performed in a series of 5 samples and 1 blank. Ultrapure water and thoroughly extracted hair and nails were used as blanks for the three matrices and the blanks were subtracted from all results. Bovine serum and thoroughly extracted hair and nails were spiked with target analytes for recovery tests (n=4). Internal standards were used for quantification. The LOD of 11 PFAAs ranged from 0.09 to 0.41 ng·mL^{-1}. The recoveries of 11 PFAAs ranged from 83 % to 116 % in bovine serum, 76 % to 137 % in hair and 68 % to 130 % in nails. All statistical analysis was performed using SPSS 13.0 and the figures were constructed with Origin 6.0.

3. RESULTS

3.1 TF, EOF and IF levels in serum, hair and nails

The mean TF, EOF and IF were 0.28, 0.21 and 0.020 μg·mL^{-1} in serum, 2.0, 0.55 and 0.044 μg·g^{-1} in natural hair, 3.9, 0.76 and 0.06 μg·g^{-1} in treated hair, 4.2, 1.6 and 0.047 μg·g^{-1} in nails. TF, EOF and IF in serum are significantly lower than in natural hair (p<0.01), dyed or permed hair (p<0.05) and nails (p<0.01). TF and EOF in nails are significantly higher than in natural hair (p<0.01). Serum IF in Shenzhen is significantly higher than in Guangdong rural area (p<0.01). TF, EOF and IF in dyed or permed hair are significantly higher than in untreated hair (p<0.05).

3.2 PFAAs residues and distributions in serum, hair and nails

The detection rate of serum PFAAs range in the order of PFOS = PFHxS = PFOA (100%) > PFDA (95%) > PFNA (93%) > PFUdA (75%) > PFDoA (70%) > PFTrDA (68%) > PFHpA (39%) > PFHxA (33%). Short- and medium-chain PFAAs are the main residual species, accounting for 96% of ∑PFAAs. Hierarchical analysis showed that in human serum, PFOS（R^2=0.2246）and PFOA（R^2=0.1848）are the typical residues of PFSAs and PFCAs, respectively. In addition, the levels of serum PFOS, PFOA, PFUdA in Shenzhen are significantly higher than in Guangdong rural areas (p<0.01), while the levels of serum PFOS, PFHxS, PFUdA and PFTrDA in males are significantly higher than in female (p<0.01).

Long-chain PFAAs were not detected in hair and nails, while short- and medium-chain PFAAs, including PFOS, PFOA, PFHxS, PFHxA and PFOS, PFOA, PFHxS, PFHpA, PFPeA, are the main

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residual species in hair and nails respectively. Moreover, hierarchical analysis showed that PFOS is the predominant PFAAs in hair (R^2=0.3714) and nails (R^2=0.4143). Nail PFOS (p<0.05) and PFHxS (p<0.01) in Shenzhen are significantly higher than in Guangdong villages, PFOA (p<0.05) in permed or dyed hair is significantly higher than in untreated hair. No other significant differences were discovered.

PFOS and PFOA in nails are significantly higher than in serum (p<0.01) and hair (p<0.01). In hair, PFHxS is significantly higher than in serum (p<0.01) and nails (p<0.01), while PFOS and PFHxA are significantly higher than in serum (p<0.01). Such significant differences were not shown by other PFAA.

3.3 Spearman correlation among TF, EOF, IF and PFAAs in serum, hair and nails

We compared the average concentrations of TF, EOF, IF and PFAAs in serum, untreated hair and nails. There are significant positive correlations among TF, EOF, IF in serum (p<0.01), as well as between TF and EOF in nails (p<0.05). In serum, there are significant positive correlations between PFOS and PFHxS (p<0.05), as well as between PFOS and PFOA (p<0.01). In serum, PFOA also significantly correlates with PFNA, PFDA, PFUdA (p<0.01), respectively. Similarly, we observed positive correlation between PFOS and PFHxS in untreated hair (p<0.05). Moreover, PFOS in nails has positive correlation with PFHxS (p<0.01) and PFPeA (p<0.05), while PFPeA positively correlates with PFHpA (p<0.05). The correlations among TF, EOF, IF and PFAAs in the three matrices are compared. PFOA in serum and untreated hair (p<0.05), PFHxS (p<0.01), PFOS (p<0.01), PFOA (p<0.05) in serum and nails, as well as TF (p<0.01), EOF (p<0.05), IF (p<0.05), PFOS (p<0.05) and PFOA (p<0.05) in natural hair and nails, are all positively correlated.

4. DISCUSSION

The residues of fluorinated chemicals in Guangdong serum distribute in the order of TF>EOF>>IF. About 70 % of fluorinated chemicals in serum exist as EOF, corresponding with the level of organic fluorine in serum, which ranges between 73 % [7] and 85 % [8]. The fluorides in hair and nails exist in the order of TF>EOF>>IF, corresponding to their distribution in serum. However, differing from in serum, EOF in hair and nails are secondary compositions making 11 % to 41 % of TF. Fluorine in human body participates in transportation as ions, mainly congregating in bones and teeth. Fluoride ion combines with Ca^{2+}, Mg^{2+}, etc, and deposit in hair and nails, resulting in high level of inorganic fluorine in these tissues [9]. In serum, hair and nails from Guangdong, IF makes 4.6 % to 33 % of EOF, leaving 67 % to 95 % of EOF as unidentified fluorine.

Among the three matrices, TF and EOF are distributed in the order of nails > untreated hair > serum, while IF is distributed in the order of nail ≈ hair > serum. Hair and nails consist of keratin. The nutrients they need are supported by hair follicles and nail bases rich in capillaries. The metabolic rates of hair and nails are much lower than that of serum, while PFAAs mainly bind with proteins. This leads to higher EOF and IF in hair and nails than in serum.

PFAAs in serum, hair and nails mainly exist in short- and medium-chains, while the detection rate of long chain PFAAs is low. This might be caused by: 1) long-chain PFAAs have low volatility and solubility, so are difficult to enter the environment and human body. 2) long-chain PFAAs tend to degrade into medium or short chains, which are more stable. In the three matrices, PFOS, PFOA and PFHxS are the typical remaining species, making 41 % to 80 %, 8 % to 37 % and 5 % to 35 % of ∑PFAAs, respectively. This corresponds with the reference reports [10, 11]. Compared to PFCAs, PFSAs accumulate more easily in organisms of high trophic levels [12]. PFOS also has longer half life (5.4 years) than PFOA (3.8 years) [13]. Therefore, PFOS is higher than PFOA in serum, hair and nails.

The serum PFOS (p<0.01), PFOA (p<0.01) and PFUdA (p<0.01), as well as the nail PFOS (p<0.05) and PFHxS (p<0.01) in Shenzhen are significantly higher than those in Guangdong villages. This could be caused by various diets and residence environments. Compared to rural

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populations, Shenzhen citizens use more modern textiles, cookers, electronic devices and makeup, as well as more packaged food and seafood, raising the exposure to PFAAs. Guruge [14] noted that industrial pollution with limited purification, as well as more developed lifestyle, adds to the risk of PFAAs exposure. Meanwhile, Hanssen [15] noticed that various life conditions, residences and diets between rural and urban areas are one of the reasons for city serum PFAAs being higher than villages. The difference in Guangdong serum PFAAs between genders shows that PFHxS, PFOS, PFUdA and PFTrDA are significantly higher in male than in female ($p<0.01$), which can be related to women's menstrual bleeding [16, 17] and the higher alcohol intake among men. Melzer [18] measured PFAAs in nearly 4000 serum samples in America and found that PFOS and PFOA in serum is apparently related to alcohol intake ($p<0.01$). Among males, The PFOS remain was also found significantly higher in drinkers than non-drinkers.

Dyes and perm agents usually contain PFAAs. The dyeing and perming of hair open hail scales to let the agents in. PFOA is more filtrating than PFOS [19], which causes higher PFOA level in treated hair than in untreated hair ($p<0.05$).

Concurring with previous reports [10, 20], the PFOS and PFHxS in serum, hair and nails are positively correlated ($p<0.05$), indicating that they have similar exposure channels, or that PFOS can degrade into PFHxS under light [21]. Meanwhile, PFOA is positively correlated to PFPeA and PFHpA in serum, hair and nails ($p<0.01$). This is due to the FTOHs in body degrading into PFOA [22], which further degrades into PFAAAs of C4-C7 [23]. Corresponding to Justina's report [24], PFOS and PFOA in serum have significant positive relationship ($p<0.01$). The reasons include: 1) the production and application of PFAAs surface reagents release chemicals like N-EtFOSE and FOSA, which could degrade into PFOS and PFOA [25, 26]; 2) breathing is an important intake channel for PFAAs, while researches discovered that PFOS and PFOA in indoor air and dust are positively related ($p<0.05$) [27].

Currently, blood is the usual sample for human PFAAs analysis. However, blood sampling is limited by law and inconvenient for large-scale exposure assessments. The typical PFAAs remain in nails are PFOS, PFOA and PFHxS, same as in serum. Meanwhile, PFHxS ($p<0.01$), PFOS ($p<0.01$) and PFOA ($p<0.05$) in nails are positively correlated to those in serum, and are significantly higher ($p<0.01$). Because PFAAs have much lower metabolic rate, as well as higher and more stable remain, in nails than in blood, it is indicated that nails is a potential bio-indicator that reflects PFAAs exposure better.

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References

[1] Singer, L.; Ophaug, R. Ionic and nonionic fluoride in plasma(or serum). *Crit. Rev. Clin. Lab. Sci.* **1982**,18 (2), 111-140.

[2] Jha S. K.; Mishra V. K.; Sharma D. K.; Damodaran T. Fluoride in the environment and its metabolism in humans. *Rev. Environ. Contam. Toxicol*. **2011**, 211, 121-42.

[3] Xing H.; Timothy A S.; Raymond A. K. Binding of perfluorooctanoic acid to rat and human plasma proteins. *Chem. Res. Toxicol.* **2003**, 16 (6), 775–781.

[4] Mak Y. L.; Taniyasu S.; Yeung L. W. Y.; Perfluorinated compounds in tap water from China and several other countries. *Environ. Sci. Technol*. **2009**, 43 (13), 4824-4829.

[5] Chen Q. W.; Zhang H.; Chai Z. F.; Shen J. C.; Yang B. Residue characteristics and distributions of perfluorinated compounds in surface seawater along Shenzhen coastline. *Environ. Sci*. **2012**, 33(6), 1795-1800.

[6] Wang X. X.; Zhang R. B.; Zhang H.; Long H.; Shen J. C.; Chai Z. F.; Yang B.; Wang Y. P. Impact of biological treatment techniques on perfluoroalkyl acids emissions in municipal sewage. *Water Air Soil Pollut*. **2016**, 227, 149-159.

[7] Rigalli A.; Alloatti R.; Puche R. C.; Measurement of total and diffusible serum fluoride. *J .Clin. Lab. Anal*. **1999**, 13 (4), 151-157.

ISBN: 978-960-6865-94-7

[8] Li C. S.; Qi J. C.; Fan J. Y.; Zhang P.; Zhu D. M.; Existing forms of fluoride in serum and their interrelation. *Tianjin Medical Journal.***1986**, 2, 84-87.
[9] Spencer H.; Kramer L.; Osis D.; Wiatrowski E.; Norris C.; Lender M.Effect of calcium, phosphorus, magnesium, and aluminum on fluoride metabolism in man. *Ann. New York Acad. Sci.* **1980**, 355, 181-194.
[10] Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldous, K. M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ. Sci. Technol.* **2004**, 38(17), 4489-4495.
[11] Liu, W.; Xu, L.; Li, X.; Jin, Y. H.; Sasaki, K.; Saito, N.; Sato, I.; Tsuda, S. Human nails analysis as biomarker of exposure to perfluoroalkyl compounds. *Environ. Sci. Technol*. **2011**, 45(19), 8144-8150.
[12] Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mykiss). *Environ Toxicol Chem.* **2003,** 22 (1), 189-95.
[13] Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froehlich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. *Environ. Health. Perspect*. **2007**, 115(9), 1298-1305.
[14] Guruge, K. S.; Taniyasu, S.; Yamashita, N.; Wijeratna, S.; Mohotti, K. M.; Seneviratne, H. R.; Kannan, K.; Yamanaka, N.; Miyazaki, S. Perfluorinated organic compounds in human blood serum and seminal plasma: a study of urban and rural tea worker populations in Sri Lanka. *J. Environ. Monit*. **2005**, 7(4), 371-377.
[15] Hanssen, L.; Rollin, H.; Odland, J.O.; Moe, M. K.; Sandanger, T. M. Perfluorinated compounds in maternal serum and cord blood from selected areas of South Africa: results of a pilot study. *J. Environ. Monit.*, **2010**, 12(6), 1355–1361.
[16] Olsen, G. W.; Church, T. R.; Miller, J. P.; Burris, J. M.; Hansen, K.J.; Lundberg, J. K.; Armitage, J. B.; Herron, R. M.; Medhdizadehkashi, Z.; Nobiletti, J. B.; O'Neill, E. M.; Mandel, J. H.; Zobel, L. R. Perfluorooctanesulfonate and other fluorochemicals in the serum of American Red Cross adult blood donors. *Environ. Health Perspect*. **2003**, 111(16), 1892-1901.
[17] Jin Y. H,; Dong G. H,; Shu W. Q.; Ding M,; Zhai C.; Wang L.; Liu X.; Saitou N.; Sasaki K. Comparison of perfluorooctane sulfonate and perfluorooctane acid in serum of non-occupational human from Shenyang and Chongqing areas. *Wei Sheng Yan Jiu*. **2006**, 35(5), 560-563.
[18] Melzer, D.; Rice, N.; Depledge, M. H.; Henley, W. E.; Galloway, T. S. Association between serum perfluorooctanoic Acid (PFOA) and thyroid disease in the U.S. national health and nutrition examination survey. Environ. Health Perspect. **2010**, 118(5), 686–692.
[19] **Cao, P.; Tian, J. F. Yang, X. J.; Yan, H. T.** In vitro experiment on percutaneous absorption of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS). *Journal of Environmental & Occupational Medicine*. **2010**, 27(3), 150-152.
[20] Haug, L. S,; Thomsen, C.; Becher G. Time trends and the influence of age and gender on serum concentrations of perfluorinated compounds in archived human samples. *Environ Sci Technol*. **2009**, 43(6), 2131-2136.
[21] Park, H.; Vecitis, C. D.; Cheng, J.; Choi, W.; Mader, B. T.; Hoffmann, M. R.Reductive defluorination of aqueous perfluorinated alkyl surfactants: effects of ionic headgroup and chain length. *J. Phys. Chem.***2009**, 113(4), 690-696.
[22] Chen, J.; Zhang, P. Y.; Liu, J. Photodegradation of perfluorinated carboxylic acids by 185 nm VUV light. *Environ. Sci.* **2007**, 28(4): 772-776.
[23] Rhoads, K. R.; Janssen, E. M. L.; Luthy, R. G.; Criddle, C. S. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. *Environ. Sci. Technol*. **2008**, 42(8), 2873-2878.
[24] Bjorklund, J.A.; Thuresson, K.; De Wit, C. A. Perfluoroalkyl compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. *Environ. Sci. Technol*. **2009**, 43(7), 2276–2281.
[25] Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol*. **2004**, 38(12), 3316-3321.
[26] Martin, J. W.; Asher, B. J.; Beeson, S.; Benskin, J. P.; Ross, M. S. PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? *J. Environ. Monit.* **2010**, 12(11), 1979-2004.
[27] Haug, L. S,; Huber, S,; Schabach, M.; Becher, G.; Thomsen, C. Investigation on per- and polyfluorinated compounds in paired samples of house dust and indoor air from Norwegian homes. *Environ. Sci. Technol*. **2011**, 45(19), 7991-7998.

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Synthesis of iron(III) oxide coated bentonite clay and its performance in the defluoridation of groundwater

T. Ngulube[1*], W. Mugera[1], H. Tutu[2]

[1] Environmental Remediation and Water Pollution Chemistry Research Group. Department of Ecology and Resources Management, University of Venda, Private bag X5050, Thohoyandou, 0950, South Africa.
[2] Molecular Science Institute, School of Chemistry, University of Witwatersrand, P/Bag X4, WITS, 2050, South Africa.
*Corresponding author: Email: tholisongulube@gmail.com

Abstract

South African bentonite clay was converted into a promising adsorbent for fluoride ions after its chemical loading with iron(III) oxides. Results showed that iron(III) oxide coated bentonite clay is an alumino silicate material with a, has a surface area of 132.3018 $m^2 \cdot g^{-1}$ and quartz is the major mineral phase on the clay. A batch fluoride sorption system was applied and the system variables investigated included the following: initial concentration of the sorbate, agitation time, adsorbent dose and pH. The iron(III) oxide coated bentonite clay reduced the fluoride concentration to 0.789 mg L^{-1} from 5 mg L^{-1}. A maximum fluoride removal capacity of 1.596 $mg \cdot g^{-1}$ was recorded at an initial fluoride concentration of 80 $mg \cdot L^{-1}$, which was higher compared to the unmodified bentonite. Between the pH range of 6 and 9 the removal capacity was above 70% and the material exhibited minimal metal leaching. The adsorption kinetics fitted the pseudo second order model indicating chemisorption. The high adsorption capacity of iron(III) oxide coated bentonite clay indicates the potential use of this adsorbent for fluoride removal from aqueous media.

Keywords: fluoride; bentonite clay; iron(III) oxide; adsorption isotherms; kinetics; thermodynamics.

1. INTRODUCTION

Water is critical to life on earth and in some circumstances it can be the medium for life itself. However, reservoirs have much water that is usually altered from their original concentration by interactions with mineral weathering [1]. This alteration especially occurs in groundwater and one common example of groundwater contamination through water-rock interaction is leaching of fluoride from fluoride bearing rocks.

The World Health Organization (WHO) classifies fluoride as one of the contaminants of water for human consumption. WHO has set a guiding value of 1.5 mg/L for fluoride in drinking water [2], while the South African drinking water standard has also set the limit at 1.5 mg/L [3]. Studies done in South Africa have revealed that the occurrence of dental fluorosis in many South Africans is related to the fluoride content of groundwater used for drinking purposes [4]. Therefore, mitigation of fluorosis is a very significant area of research and needs continued attention until a reliable defluoridation technology is developed.

Several defluoridation methods including precipitation, ion exchange and membrane processes have been developed to deal with this problem [5]. However, the weaknesses of a lot of these techniques are numerous. They include high operational and maintenance costs, secondary pollution, production of toxic sludge and complex processes involved in the treatment [6]. In light of the above, consideration must be given to those methods that reduce the capital and running costs. Moreover they have to be affordable and available to small communities, especially in rural areas located in developing countries that do not have adequate and effective water treatment

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technologies. Among the above mentioned methods, adsorption is regarded as the most promising method for the defluoridation of water due to the ease of operation, lower cost and being a relatively environmentally friendly process [7].

A number of studies have been performed using raw and modified clays for the defluoridation of contaminated water [8; 9; 10; 11]. The factors found to influence fluoride sorption include solution pH, clay surface area, structure, aluminum content, and the presence of certain exchangeable cations capable of forming fluoride precipitates. Bentonite clay can sorb fluoride in acid conditions and has a high pH dependency [12; 13]. Although bentonite clay can adsorb many pollutants, its use as an adsorbent in a filtration mode is limited in practice because on contact with water, bentonite clay swells and forms a highly stable colloidal suspension, making its separation from water following adsorption very difficult [14]. Modification of bentonite is vital to increase its applicability potential for the adsorption of fluoride in a continuous flow regime. The objectives of this study are therefore: 1) to activate bentonite clay with NaOH 2) to coat bentonite clay‘s surfaces with iron (III) oxides and characterise the solid product 3) to evaluate the solid product for its water defluoridation potential.

2 MATERIALS AND METHODS

2.1 Modifying bentonite clay with NaOH and Fe_2O_3

NaOH solutions of 0.01, 0.05 and 0.1M concentrations were used to activate the raw bentonite clay and various bentonite clay masses and agitation times were optimised. The activated bentonite clay was coated by varying Fe_2O_3 concentrations of 0.1 M, 0.3 M and 0.5 M and the shaking times were varied from 1 h to 3 h and 6 h.

2.2 Physicochemical and mineralogical Characterization

Mineralogical composition of the clay was determined using a PANalytical X'Pert Pro powder diffractometer in θ–θ configuration. Elemental composition was determined using XRF (Thermo Fisher ARL-9400XP + Sequential XRF equipped with WinXRF software). Surface area was determined using BETanalysis (Micromeritics Tristar II, Norcross, GA, USA). The cation-exchange capacity of the clay was determined using the ammonium acetate method. Point of zero charge was determined by solid addition method

2.3. Batch Adsorption experiments

All the reagents used were of analytical grade (Rochelle Chemicals and Lab Equipment CC, South Africa Ltd). Fluoride stock solution (100 mg/L) was prepared by dissolving 0.221 g anhydrous sodium fluoride in 1 L of MilliQ water. This was further diluted to the desired concentrations for practical use. A known weight of the adsorbent was added to 100 mL of the desired fluoride solution in a 250 mL plastic bottle and then stirred on a reciprocating shaker at 250 revolutions per minute (rpm) at room temperature. After continuous stirring for a fixed time interval, the samples were filtered using a 0.45 µm pore cellulose nitrate membranes and the fluoride concentration in the residual solution was measured by a fluoride ion selective electrode (Thermo Scientific Orion Star A215 pH/ Conductivity Benchtop Meter (USA) coupled to a 8157BNUMD Orion ROSS Ultra Triode pH/ATC electrode). A similar ion meter coupled with a pH electrode was used for measuring pH of the treated samples. Before fluoride determination, a total ionic strength adjusting buffer (TISAB 111) was added to the solutions in a ratio of 10:1 in order to maintain ionic strength and pH, and eliminate the interference effect of F^- ion complexing metal cations. The procedures were repeated to investigate the effect of adsorbent dose, initial concentration and pH.

3. RESULTS AND DISCUSSION

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3.1 Modifying bentonite clay: Optimisation of reaction conditions

Optimization of conditions of activating bentonite with NaOH was performed using batch experiments and the following conditions were established: (60 min contact time, 1 g dosage and 0.01 M NaOH concentration)

On the basis of BET results, it was concluded that 0.5 M $FeCl_3$ and 6 h of agitation time were the optimum conditions of coating the NaOH activated bentonite clay with iron oxides since these conditions gave the highest surface areas of the clay. The NaOH activated bentonite had a BET Surface Area of 60.2992 m^2/g. Upon modification with $FeCl_3$ the surface area increased by approximately 41%.

3.2 Characterisation of the adsorbents

3.2.1 Cation Exchange Capacity (CEC), Point of Zero Charge (PZC) and Brunauer Emmet Teller (BET) analysis

Table 1 shows the characterisation results of CEC, PZC and BET surface area of the raw and modified bentonite clay.

Table 1: CEC, PZC and BET surface area of the raw and modified bentonite clay.

	Raw bentonite clay	**Iron(III) oxide coated bentonite**
CEC	142.04(meq/100g)	88.9(meq/100g)
PZC	8.8	7.5
BET surface area	43.2077(m²/g)	132,3018(m²/g)

Comparing the CEC of the iron(III) oxide coated and raw bentonite clay it can be seen that after modification the CEC was greatly reduced meaning that the exchangeable cations were exchanged for the trivalent Fe^{3+} during the modification stage with $FeCl_3$.Iron(III) oxide coated bentonite has a PZC at pH 7.5 which is slightly lower than that of the raw bentonite .A PZC at 7.5 means that adsorption of fluoride using iron(III) oxide coated bentonite clay is effective in acidic conditions since the surfaces of the clay will be positively charged at that pH range. The BET surface area of the raw bentonite and iron(III) oxide coated bentonite was observed to be 43.2077 and 132.3018 m^2/g respectively. As shown in Table 1, the coatings of iron oxide substantially changed the surface area of the raw bentonite clay. The BET surface area of the iron(III) oxide coated bentonite was more than that of the raw bentonite and it increased by a factor of $\approx$ 3 which may be due to the upsurge of the clay interlayers by the iron oxides/hydroxides precipitates formed during modification this resulting in the expansion of pore interlayer spaces of bentonite clay eventually leading to the increased surface area

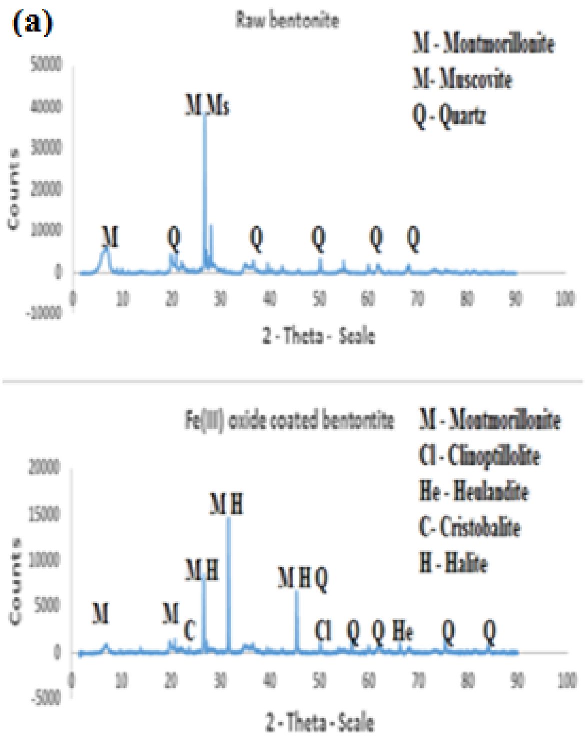
3.2.2 X – Ray Diffraction (XRD) and X – Ray Fluorescence (XRF) analysis

Figure 1(a) and (b) shows the mineralogical and elemental composition of the raw and modified bentonite clay.

The XRD pattern of both raw bentonite and iron(III) oxide coated bentonite clay (Figure 1(a)) suggests that the clays are highly crystalline and have quartz and montmorillonite as the major mineral components. XRF analysis (Figure (1b)) recorded an appreciable amount of SiO_2 and Al_2O_3 for both raw bentonite and iron(III) oxide coated bentonite clay suggesting that this clay is an aluminosilicate. However upon modification the amount of Al_2O_3 was reduced. Most of the Al dissolved during the activation of bentonite with NaOH hence the decrease of Al_2O_3. A notable increase is shown in Fe_2O_3 percentage. This is to be expected because the clay was modified by coating it with iron oxides.

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(a)



(b)

Elements as oxides	% W/W (Raw)	% W/W (MB)
Al_2O_3	14.04	8.80
CaO	0.93	0.37
Cr_2O_3	0.00	0.02
Fe_2O_3	3.31	28.35
K_2O	1.01	0.70
MgO	2.68	1.64
MnO	0.05	0.09
Na_2O	2.69	8.99
P_2O_5	0.06	0.05
SiO_2	58.84	37.33
TiO_2	0.47	0.18
L.O.I	14.79	14.44
TOTAL	**98.87**	**100.96**

Figure 1 (a) Mineralogical composition
(b) Elemental composition of the raw and modified bentonite clay**.**

3.3 Batch adsorption experiments: Optimisation of fluoride adsorption conditions

3.3.1 Effect of contact time

The removal of fluoride as a function of contact time is shown in Figure 2 (a). It was observed that the % removal increases with increase in contact time until 30 min. The theoretical explanation to this trend can be ascribed to the number of active site on the adsorbents. The fast adsorption rate at the initial stage is likely due to the availability of a large number of active sites on the adsorbent surface.

3.3.1 Effect of adsorbent dosage

The effect of adsorbent dose on F^- adsorption was evaluated at room temperature using 3 different initial F^- concentrations (Figure 2b) and a direct proportional trend was observed between dosage and % removal. The increase in the fluoride removal with dosage of the adsorbent is likely driven by the enhanced availability of active sites. The maximum F^- removal was observed with 3 g adsorbent dose at all initial fluoride concentrations. It was noted that a further increase in the absorbent dosage did not considerably change the removal capacity.

3.3.2 Effect of initial fluoride concentration

The effect of initial concentration on fluoride removal is shown in Figure 2(c). It is observed that the percent of the adsorbed fluoride ions decreases with increase in the fluoride concentration which indicates that adsorption depends upon the availability of binding sites for fluoride ions. When the initial fluoride concentration is 5 mg/L, with 3 g adsorbent dose, the equilibrium concentration of fluoride is reduced down to below the level of 1.5 mg/L under the current experimental conditions, which approaches the DWS drinking water standards of fluoride concentration.

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3.3.3 Effect of pH

Figure 5(d) shows that there was high F^- adsorption observed at pH 2 which gradually decreased with an increase in the initial pH of the solution. Several dominating factors might be responsible such a trend. One factor is related to the production of the fluoride complex at acidic or basic media. The second factor responsible for fluoride removal might be through ligand exchange type interactions between the hydroxyl groups and fluoride leading to reduced fluoride removal when pH increases because of a higher concentration of OH ions.

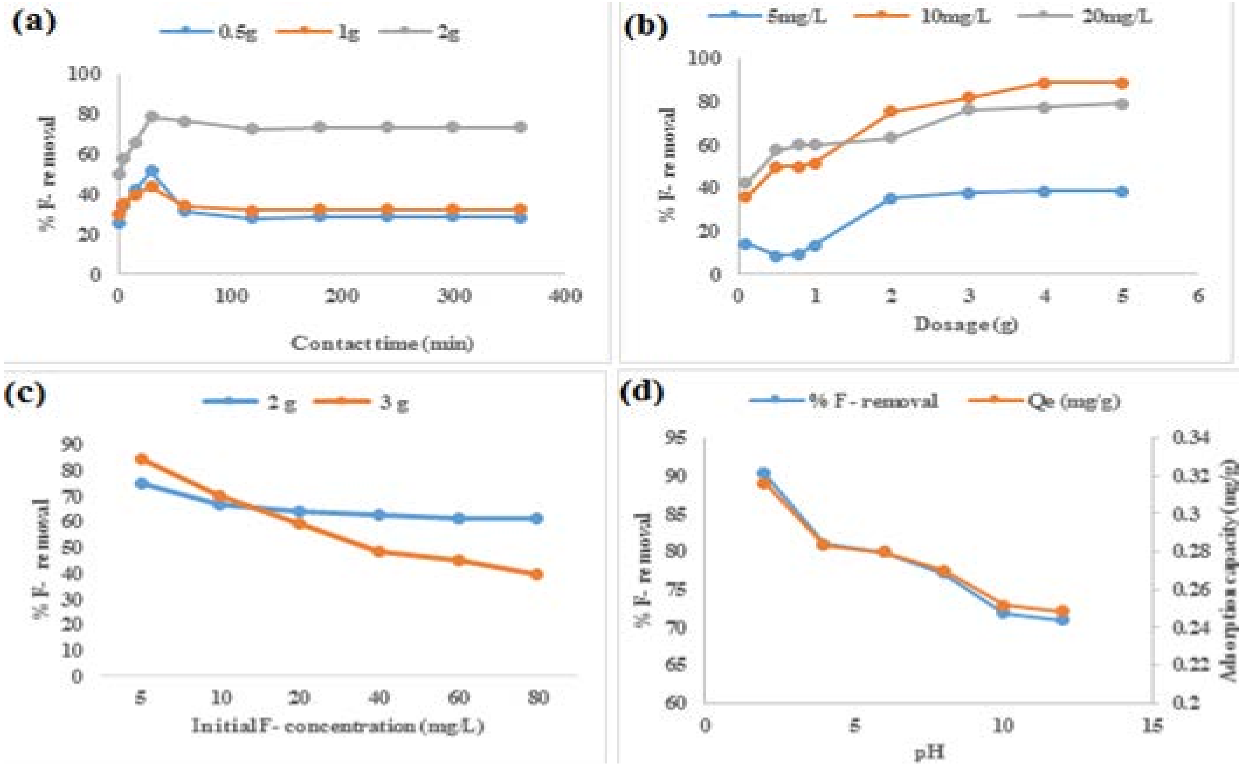


Figure 2: (a) Effect of contact time (0.5, 1 and 2 g , 10 mg/L F^- , 25ºC, 100 mL (a) 250 rpm, pHi = 6.653) (b) Effect of dosage (30 min , 5, 10, 20 mg/L F^- , 25ºC, 250 rpm pHi = 7.434) (c) Effect of F^- initial concentration (30 min, 2 and 3 g, 25ºC , 100 mL, 250 rpm pHi = 6.263) (d) Effect of pH (30 min, 5 mg/L F^- , 25ºC, 3 g/100 mL S/L ratio, 250 rpm)

3.4 Treatment of raw fluoride water from Siloam, Limpopo province, South Africa borehole at pH optimized conditions

Table 2 shows the physicochemical characteristics of the borehole water samples before and after defluoridation.

As shown in Table 2, all the measured parameters besides fluoride were within the DWS water quality guidelines when the defluoridation was performed at both field pH and optimised pH conditions. However the fluoride removal efficiency was higher at optimised conditions. The percentage fluoride removal at field conditions is 31% whereas at optimised conditions the fluoride removal is 71%. The lower % F^- removal for field water at field conditions could be due to the effect of co-existing ions which competed for adsorption sites with F^-. It is expected that the presence of anions in solution would enhance coulombic repulsion forces between the anions and fluoride or would compete with fluoride for the active sites [15].

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Table 2: Adsorption of fluoride by iron(III) oxide coated bentonite clay under field and optimized conditions.

Parameter	Siloam borehole water	Field pH (pH = 7.81)	Optimized pH (pH = 2. 12)	DWS guidelines
pH	7.81	7.624	7.11	6 – 9
EC (µS/cm)	25.74	25.12	25.10	0 – 150
F^- (mg/L)	5.53	4.233	3.23	1 – 1.5
Cl^- (mg/L)	31.6	180.1	189.1	0 – 250
SO_4^- (mg/L)	11.9	N.D	N.D	0 – 250
Br^- (mg/L)	2.08	N.D	N.D	0 – 6
NO_3^- (mg/L)	1.13	N.D	N.D	0 – 6
PO_4^{3-} (mg/L)	ND	N.D	N.D	0 - 5

3.5 Adsorption kinetics

The kinetics of adsorption controls the efficiency of the process and the equilibrium time. It also describes the rate of adsorbate uptake on the adsorbent. To identify the potential rate controlling steps involved in the process of adsorption, two kinetic models were studied and utilized to fit the experimental data from the adsorption process. These models are the pseudo- first-order and the pseudo-second-order models.

3.5.1 The pseudo first-order equation

The pseudo first-order equation (Lagergren's equation) describes adsorption in solid–liquid systems based on the sorption capacity of solids [16].
The linear form of pseudo first order model can be expressed as

$$\log(q_e - q_t) = \log q_e \ - (\frac{K}{2.303})t \dots\dots (1)$$

Where qe (mg/g) is the adsorption capacity at equilibrium, qt (mg/g) is the adsorption capacity at time t, and K (1/min) is the rate constant of pseudo-first-order. The value of K can be obtained from the slope by plotting log (qe – qt) vs t.

3.5.2 Pseudo second order kinetics

The pseudo second-order rate expression, which has been applied for analyzing chemisorption kinetics from liquid solutions pseudo-second based on solid phase sorption is linearly expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e} + (\frac{1}{q_e})t \dots\dots (2)$$

where k_2 is the rate constant for pseudo second-order adsorption (g/mg/h) $k_2qe$or h (mg/g/h) is the initial adsorption rate.

The parameter values obtained by curve-fitting kinetic data are listed in Table 3.

The pseudo-second-order kinetic model proved to be more suitable in describing the adsorption kinetics of fluoride based on the correlation coefficient ($R^2 > 0.99$) as shown in Table 3, suggesting that a chemisorption step might be rate determining in the fluoride adsorption process. Furthermore, it could be seen that the theoretical adsorption capacities, q_e, were all very close to the experimental capacity. Similar results were observed for the adsorption of fluoride by various adsorbents [17, 18]

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Table 3: Pseudo-second-order kinetic parameters for different adsorbent dosages for fluoride removal by iron(III) oxide coated bentonite clay

Dosage (g)	qe exp (mg/g)	K_2(gmh)	qe cal (mg/g)	R^2
0.5	0.34	1.4082	0.2205	0.9994
1	0.44	1.2554	0.3203	0.9997
2	0.44	3.9003	0.4232	1

4. CONCLUSIONS

Based on the experimental data, the equilibrium adsorption is practically achieved in 30 min.

Solution pH played a major role in fluoride removal by iron(III) oxide coated bentonite clay with an optimum pH being pH 2. High adsorption >70% was observed over the pH range 2-12 which is significant for application in defluoridation of groundwater whose pH is circumneutral. The pseudo-second-order kinetic model could be used to describe the fluoride adsorption behaviours and both intra and external diffusion regulated the adsorption process.

From the results, we can conclude that iron(III) oxide coated bentonite clay is a promising sorbent for defluoridation of water.

References

[1] Banks D, Reimann C, Røyset O, Skarphagen H, Sæther OM. 1995. Natural concentrations of major and trace elements in some Norwegian bedrock ground waters. *Appl Geochem*, **10,** 1–16.

[2] WHO. 2004. Guidelines for drinking-water quality. 3rd Ed .World Health Organization, Geneva, 375–378, 301–303.

[3] DWAF. 1996. South African Water Quality Guidelines for Domestic Use .1st Ed.

[4] WRC. 2001. Distribution of Fluoride-Rich Groundwater in the Eastern and Mogwase Regions of the Northern and North-West Province. WRC Report No. 526/1/01 1.1 - 9.85. Pretoria. South Africa.

[5] Zeni M, Riveros R, Melo K, Primeri R, Lorenzini S. 2005. Study on fluoride reduction in artesian wells-water from electrodialysis process. *Desalination*, **185,** 214-244.

[6] Bhatnagar A, Kumar E, Sillanpaa M. 2011. Fluoride removal from water by adsorption-A review. *Chem Eng J*. **10,** 5 - 28.

[7] Thakre D, Rayalua S, Kawadea R, Meshramb S, Subrtc J, Labhsetwara N. 2011. Magnesium incorporated bentonite clay for defluoridation of drinking water. *Journal of Hazardous Materials*. **180,** 122–130.

[8] Daifullah AAM, Yakout SM, Elreefy SA. 2007. Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw. *Journal of Hazardous Materials*. **147,** 633–643.

[9] Gitari WM, Ngulube T, Masindi V, Gumbo JR. 2013. Defluoridation of groundwater using Fe^{3+} -modified bentonite clay: optimization of adsorption conditions. *Desalin Water Treat*. 1578–1590.

[10] Jiang J, Zeng J. 2003. Comparison of modified montmorillonite adsorbents. The effects of the type of raw clays and modification conditions on the adsorption performance. *Chemosphere*. **53.** 53–62.

[11] Masindi V, Gitari WM, Ngulube T. 2014. Defluoridation of drinking water using Al^{3+} -modified bentonite clay: optimization of fluoride adsorption conditions. Toxicol Environ Chem. **96 (9),** 1294–1309.

[12] Tor, A., 2006. Removal of fluoride from an aqueous solution by using montmorillonite. *Desalination*, **201**, 267 – 276.

[13] Kau PMH, Smith DW, Binning P. 1997. Fluoride detention by kaolin clay. *J. Contamin. Hydrol*, **28**, 267–288.

[14] Kapoor A, Viraraghavan T. 1998. Use of immobilized bentonite in removal of heavy metals from wastewater, *J. Environ. Eng. ASCE*, **124**, 1020–1024.

ISBN: 978-960-6865-94-7

[15] Onyango MS, Kojima Y, Aoyi O, Bernardo EC, Matsuda H. 2004. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, J. *Colloid Interface Sci*. **279**, 341–350.
[16] Ho Y.S, Wase DAJ, Forster CF. 1995. Batch Nickel removal from aqueous solution by Sphagnum moss peat. *Water Research*, **29 (5),** 1327–1332.
[17] Cai H, Chen G, Peng C, Zhang Z, Dong Y, Shang G, Zhu X, Gao H, Wan X. 2015. Removal of fluoride from drinking water using tea waste loaded withAl/Fe oxides: A novel, safe and efficient bio sorbent. *Applied Surface Science*, **328,** 34–44
[18] Tchomgui-Kamga E, Alonzo V, Nanseu-Njiki CP, Audebrand N, Ngameni E, Darchen A. 2010. Preparation and characterization of charcoals that contain dispersedaluminum oxide as adsorbents for removal of fluoride from drinking water, *Carbon*, **48**, 333–343.

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Traffic noise in mid-size towns: The case of Xanthi, Northern Greece

G. Kollaros*, A. Athanasopoulou, V. Kollarou

Department of Civil Engineering, Democritus University of Thrace, 67132, Xanthi, Greece.
*Corresponding author: Email: gkoll@civil.duth.gr

Abstract

Noise emitted from various sources has high priority on lists of environmental issues in Europe and noise reduction has increasingly become a focus for EU legislation. In urban areas, traffic noise is generated from three basic sources, the engine block, the exhaust system and the contact between the tire and the road. The type of vehicles, the traffic volumes and the types of land development in the area surrounding the road axes play an important role in estimating the cost of damages due to traffic noise in residential areas. A social inquiry among Xanthi's residents has been simultaneously conducted with traffic counts and noise level measurements. Good correlation among the parameters has been found. If the sound level of the road noise is very high, the annoyance caused requires special protection of the receivers. To ensure that people are not disturbed by traffic noise in their homes sufficient sound insulation from the external noise should be provided.

Keywords: noise; noise-abatement; swelling buildings; traffic; environmental impacts

1. INTRODUCTION

With the growth of cities, roads with more flow capacity are needed. As a result, the emitted noise shows increased levels [1, 2, 3]. The noise generated by the movement of vehicles in the streets and roads, implies discomfort to roadside residents most exposed to it [4]. This annoyance results from many different (physical, physiological, psychological, etc.) causes making the definition of "annoyance" extremely difficult. If the sound level of the road noise is very high, the annoyance caused requires special protection of the receivers [5]. It is also known that any increase of the noise level constitutes an analogous downgrading of life quality. For educational activities, the ambient noise levels are of great importance [6], as the intelligibility of speech in rooms is fundamental for a good process of learning. On the other hand, an environment without these qualities can be an obstacle for education.

Road traffic noise significantly contributes to environmental noise. In the 2007 CE Delft report it was estimated that almost 210 million EU citizens are exposed to 55 decibels (dB) or more of road noise [7]. Road traffic is the main source of noise in residential areas and its assessment and management is, therefore, strictly linked to such issues. For this reason, monitoring traffic and noise in urban areas has been the object of many studies, and their results have been used to build up noise maps to determine the population exposure to environmental noise [8].

In 2012, the medium sized cities of Volos and Larissa in central Greece completed their strategic noise maps and relevant action plans in the framework of the European Directive 2002-49-EU [9] that defines the main strategies to reduce noise exposure of residents and introduce and preserve "quite zones". Due to their proximity to transportation infrastructures, 4 districts in Volos and 1 in Larissa were representative of urban situations and of different urban typologies (downtown area with or without shops, residential district, densely populated neighbourhood) [10].

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A sociological survey on sound and noise perception has been performed between the residents using questionnaires. Through qualitative criteria, a soundscape analysis was also conducted. Abatement measures have been suggested on the basis of the findings of this research.

Pamplona is a medium-sized city located in the north of Spain. The old part of the city has very narrow streets, open to road traffic. An extensive noise survey was carried out in the city [11]. This work yielded a detailed daytime acoustic map of the city. The study included a social survey in five representative areas of the city to assess the degree of noise annoyance in the community and its relationship with the measured noise levels. The social survey showed that noise annoyance is a serious problem for the residents (very high percentages of people suffering from sleep disturbance).

A simplified traffic noise mapping method was applied to Valdivia, a small city in Chile. The success was full supported by an analysis of road traffic (involving the separation of light and heavy vehicles, and motorbikes and noise levels and noise levels. Eighty measurement locations were chosen on different road types without exceeding 5% gradients were chosen. The traffic flow information was obtained in-situ [12].

In 2005, a study was carried out to determine motorway noise levels in the centre part of Tokat city, located at northern Turkey. Due to the rapid increase in the number of vehicles, noise pollution has reached important levels. In six or seven streets noise exceeded 65 dB(A) with the highest value reaching 77 dB(A) [13].

Curitiba is the capital and largest city of the Brazilian state of Paraná (1,879,355 people as of 2015). People has migrated from the country to find jobs in automobile industries, construction manufactures etc. The increasing number of living people and vehicles has led the University to add noise pollution as new subject to the curriculum [14]. A noise survey in 1,000 sites has shown that during daytime equivalent sound levels were over 75 dB(A) in about 40% of the sites.

2. ROAD NOISE, RESIDENCY AND HUMAN ANNOYANCE

The impacts of road traffic noise on residents could be sufficiently predicted by known metrics, such as the Leq, Ldn, and Lden (equivalent noise level, day–night level, day–evening–night level). [15]. Leq is the preferred method to describe sound levels that vary over time, resulting in a single decibel value which takes into account the total sound energy over the period of time of interest.

The environmental noise caused by traffic can reduce the value of the residential property [16]. The procedure through which the reduced housing value could be estimated must take into consideration noise from vehicles, based on theories that people will pay to avoid high noise levels and that housing values reflect location relative to a noisy roadway. Three major components include:

(1) the number of affected housing units, which varies by location,
(2) the noise level in decibels above an established noise threshold, which changes depending on the type of vehicle, its speed, its operating weight, and the volume of traffic on the roadway, and
(3) the average change in property values per decibel that can be attributed to the roadway, which is constant for all housing units.

It is known that any increase of the noise level constitutes an analogous downgrading of life quality. Any increase in noise level is proportional to the deterioration of living conditions. Besides residency, another social value impacted by traffic noise in medium sized cities is education. For educational activities, the ambient noise levels are of great importance, as the intelligibility of speech in rooms is fundamental for a good process of learning [17, 18]. Considering different types of noise, evidence has been presented of aircraft noise being particularly disruptive to learning, traffic noise less disruptive but still impairing performance, while train noise did not cause a problem [19]. On the other hand, an environment without these qualities can be an obstacle for

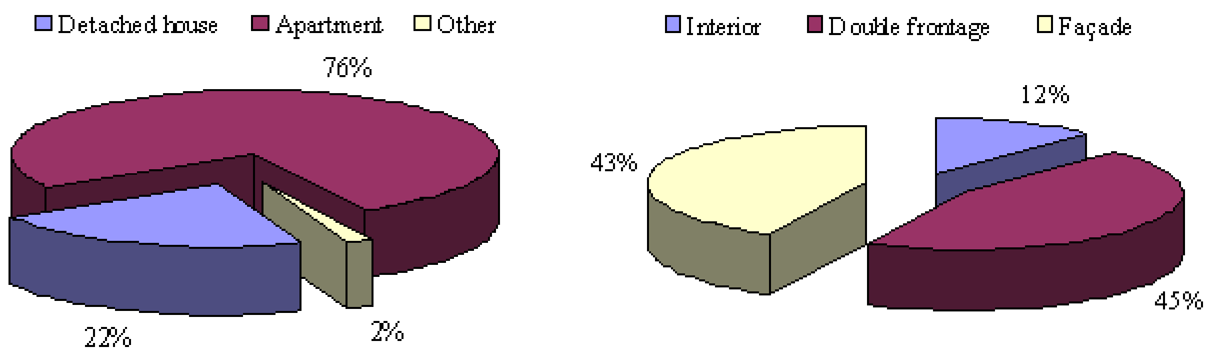
education. Many factors contribute to this discomfort in school classrooms (physical, physiological, psychological), making the precise definition of the concept of annoyance extremely difficult.

3. TRAFFIC NOISE IN XANTHI'S RESIDENTIAL AREA

An extended survey conducted in the central part of Xanthi, Northern Greece, revealed that traffic noise constitutes a problem for the residents in the area. The city of Xanthi has moderate traffic problems and the circulation of vehicles is rather easily accomplished. The vehicle fleet is composed mainly of private cars and small vans. However, citizens often complain about traffic noise. This could be attributed to the geometric characteristics of streets and the arrangement of buildings across them. A good relationship between the traffic measurements and the expected noise levels has been found. A variety of possible noise mitigation measures can reduce the noise impact of the existing roadway network.

Residents in the surveyed area were called to answer a questionnaire comprised of five parts. The questions in the first part related different personal characteristics such as the age, the profession and the level of education. Data about the type of the building and the state of economics of the household were collected in the second part of the questionnaire. Part three asked the habitants to characterize their neighbourhood and to point out the most serious problems. The effects of the most important sources of noise were investigated in part four. In part five, the person who answered the questionnaire gave his/her opinion about the noise in his/her working place, if he or she is occupied outside the house. It must be noticed that most of the persons who responded to the questionnaire live in the area for several years.

The dwellings in the investigated area were divided in three categories; namely, apartments, detached houses, and other types. Apartments were further distinguished to interior, façade, and double frontage ones. The majority of the dwellings were apartments, a fact that greatly represents the character and pattern of the area, since it is a central part of the town where many apartment buildings exist. The different categories of houses are shown in Figure 1 along with their merits to the total number of housings (in percentages).



(a) Dwellings in the surveyed area

(b) Apartment types

Figure 1. Distribution of dwellings and various apartment types of in the central area of Xanthi

In the literature, a large number of noise forecasting models, referring to different types of roads (urban roads, motorways, and so on), is reported. Such models generally consist of empirical equations which allow calculations of noise levels associated to traffic flow showing determined composition (heavy vehicles, motorcycles, cars) and characteristics (speed, flow, etc.). Traffic counts have been made on the road network of the City of Xanthi in order to reveal the relation of traffic synthesis and volume and noise in urban area. Figures 2 and 3 present traffic count data for a

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typical working day for passenger cars, and trucks and buses, respectively. Some peaks have appeared which are justified by movements of employed people to and from their jobs or working places. Because of the size of the city, bicyclists cover a large percentage in the traffic mix. In Figure 4 the results of a 16-hour count of bicycles and motorbikes show a peak between 13:00 and 15:00, in agreement with the rest traffic peaks.

Measuring environmental noise in practical situations is complicated due to noise from intervening human activities, variations in noise situations from day to day and requirements for noise-source specific measurement results. Noise measurements have been carried out during the nighttime at 2 discrete locations in Xanthi (busy from a traffic flow view intersections). The instruments were positioned at a height of about 4 meters, considering the first floor apartments have their balconies at that level. The season of the year was early spring (March). The main scope of the noise survey was to test the effect of traffic on sleep disturbance. Noise charts, as printed by the noise measuring instruments are shown in Figures 5 and 6. Noise levels ranged between 50 and 80 dB(A) with few exceptions. Noise metrics recorded were L1=83.3 dB(A), L10=76.1 dB(A) med Leq=72.6 dB(A) (Figure 5).

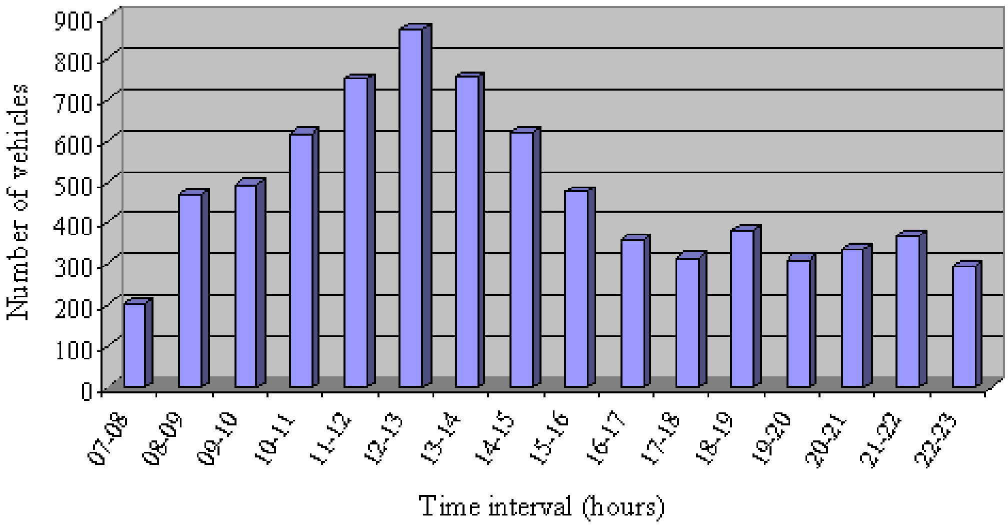


Figure 2. Private cars in traffic volume mixture

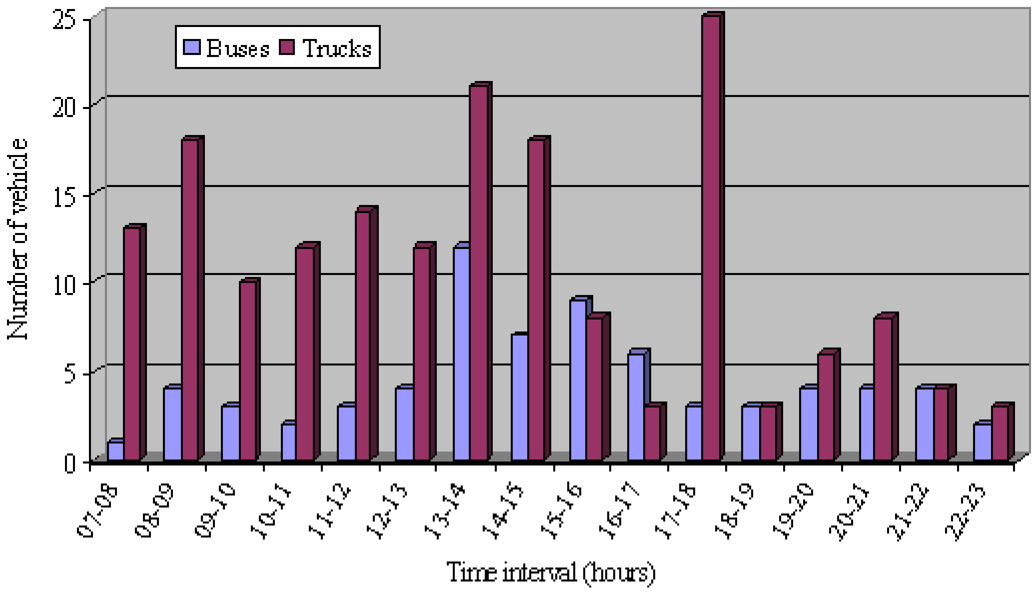


Figure 3. Traffic volume of heavy vehicles (buses and trucks)

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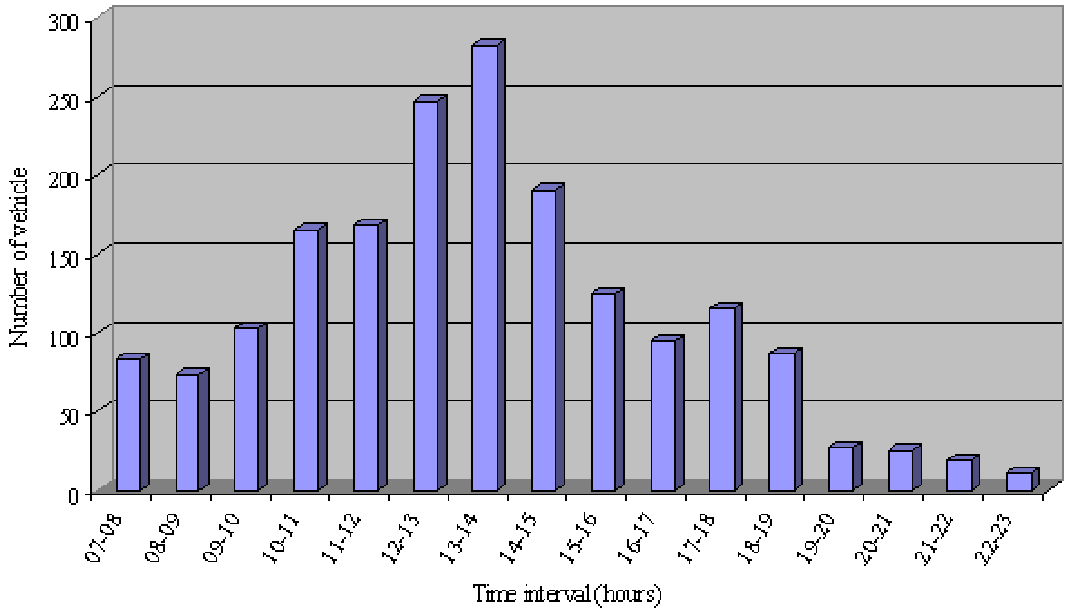


Figure 4. Traffic volume of bicycles

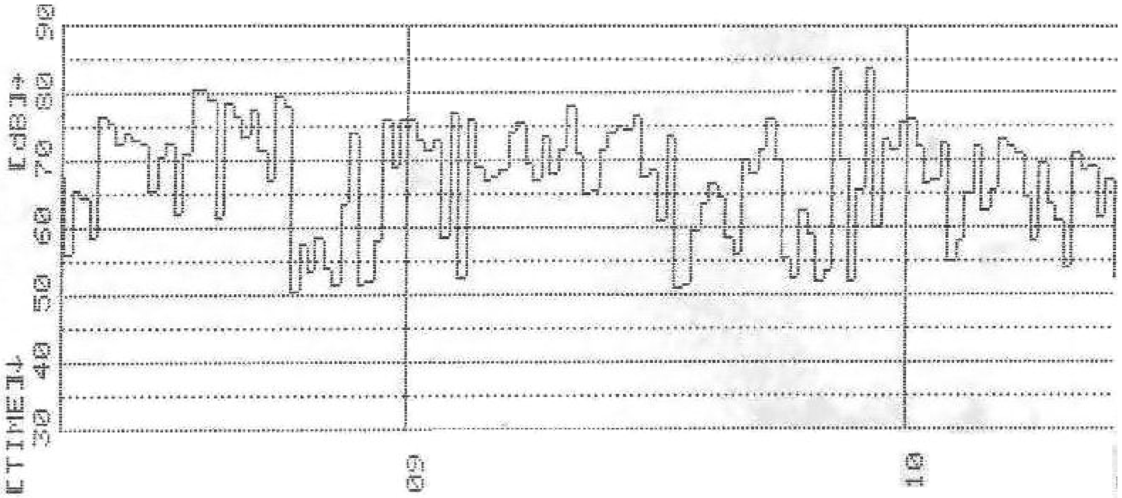


Figure 5. Nighttime noise chart at Andreou Demetriou with Pericleous Streets intersection

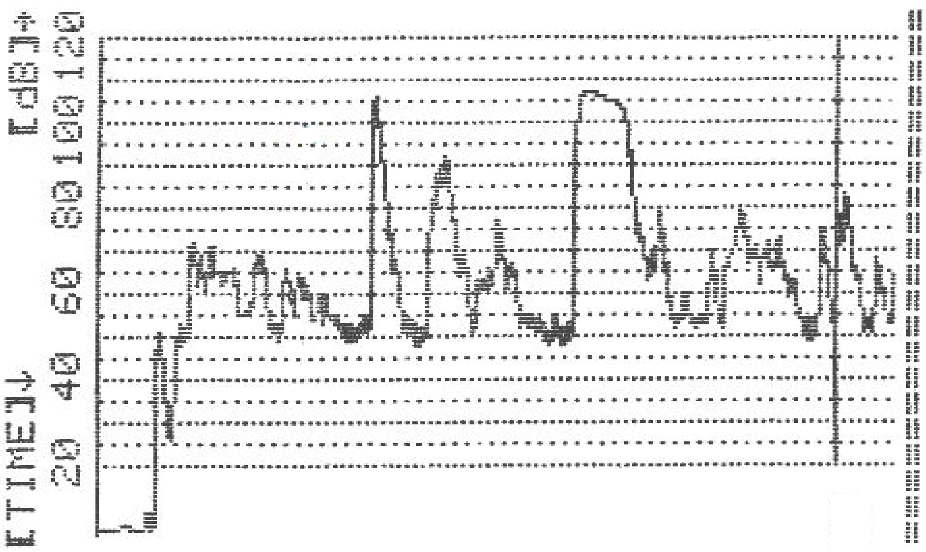


Figure 6. Nighttime noise chart at Pericleous and Sardeon Streets intersection

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4. RESULTS AND DISCUSSION

Traffic counts were conducted in 21 intersections within the area of interest. The measurements lasted 16 hours, starting at 7:00 and ending at 23:00 hours. They covered both working days and weekends. The main findings are:

- passenger cars were over 75% in the total mix in all roads covered and over 85% where turning movements are a possibility
- motorcycles have a remarkable percentage of 19%. The higher percentages were found during noon hours, mainly because students and younger workers are moving these hours. Motorcycles considered very annoying to people living in ground floors or in apartments which face the road.
- buses did not exceed the 1.0% per hour in the traffic volume
- trucks were not uniformly distributed in all roads. The larger numbers occurred in broader roads and in roads having asphalt pavements
- the peak hours were between 11:00 and 15:00 hours

There are many different sources of environmental noise to which people are exposed including: transport (road, rail, and air traffic), construction and industry, community sources (neighbours, radio, television, bars, and restaurants), and social and leisure sources (portable music players, fireworks, toys, rock concerts, etc.). Noise from all sources may be relevant to the assessment of risk, and hence it may be appropriate to assess the exposure of the population to all these sources. People responded that they don't feel annoyed to the same extent at different times. The percentages of annoyance are shown in Figure 7 for often appearing noisy events and for scarcely annoying sources during various human activities like eating, sleeping, or having leisure breaks.

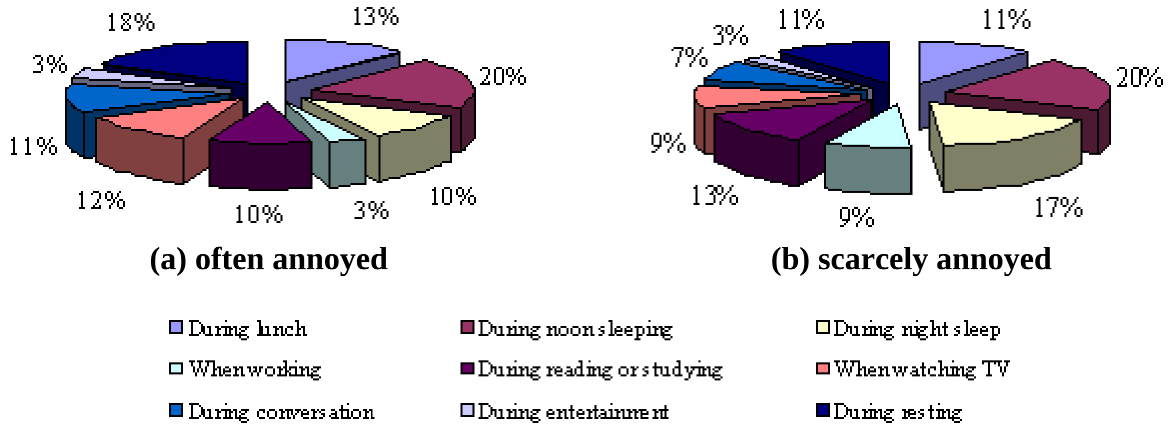


Figure 7. Frequency of annoyance due to traffic noise during different living situations

The questionnaire for the survey in Xanthi included questions on the annoyance by different sources of noise or activities related to traffic or other residents' occupations. The results in the form of percentages of persons annoyed are given in Figure 8. Building and construction activities (40%) along with traffic (30%) dominate this field of the questionnaire.

In practice, it is almost impossible to consider exposure to all sources in a risk assessment, because some exposures are difficult to estimate at the population level (e.g. leisure noise through attending music concerts). On the contrary, considerable amount of research has been devoted on assessing the exposure of population to noise sources such as traffic. For those living in roads with heavy traffic volumes, the noise annoyance is especially stressful, irrespective the height of the building, the road geometry and the characteristics of pavement.

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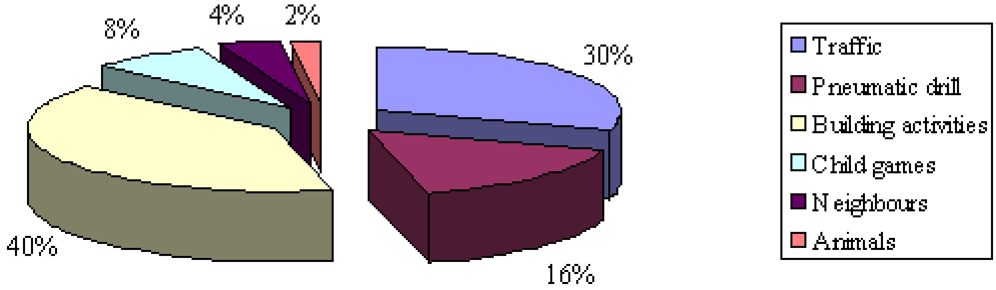


Figure 8. Percentage of people in the surveyed area annoyed by various noise sources

5. CONCLUSIONS

The goal of an engineer to either increase roadway capacity or improve traffic flow may often conflict to a neighbourhood's goal to be free of congestion, pollution, and traffic noise. The two objectives do not have to be mutually exclusive. Controversies involving traffic noise are often based on misinformation, perception, or anecdotal evidence, not on facts, good engineering, or reality.

The noise caused by the road and highway traffic annoys the residents most exposed to it. A variety of possible noise mitigation measures can reduce the noise impact of the existing roadway network. There is a need to extend the research of medium sized cities which have implemented such techniques or methods.

Environmental noise caused by traffic can reduce property values. The reduction of traffic volume is not the only means of attenuating sound pollution. Another alternative consists in moderating the traffic, i.e. to reduce the emissions of noise by lowering the speed of circulation in mid-sized cities centres. Roadways could also be covered with "quieter" asphalt material, or cars could be equipped with less noisy tires. The buildings insulation through double windows could also contribute to the solution of noise annoyance.

References

[1] Heutschi, K., 1995. A simple method to evaluate the increase of traffic noise emission level due to buildings, for a long straight street. *Applied Acoustics*, **44(3)**, 259 – 274.

[2] Chew, Y.R., Wu, B.S., 2016. A soundscape approach to analyze traffic noise in the city of Taipei, Taiwan. *Computers, Environment and Urban Systems*, **59**, 78 – 85.

[3] Huang, B., Pan, Z, Wang, G., 2015. A methodology to control urban traffic noise under the constraint of environmental capacity: A case study of a double-decision optimization model. *Transportation Research Part D: Transport and Environment*, **41**, 257 – 270.

[4] Muzet, A., 2007. Environmental noise, sleep and health. *Sleep Medicine Reviews*, **11**, 135 – 142.

[5] Olayinka, O.S., 2013. Effective noise control measures and sustainable development in Nigeria. *World Journal of Environmental Engineering*, **1(1)**, 5 – 15.

[6] Woolner, P., Hall, E., 2010. Noise in schools: A holistic approach to the issue. *International Journal of Environmental Research and Public Health*, **7**, 3255 – 3269.

[7] den Boer, L.C., Schroten, A., 2007. Traffic noise reduction in Europe. Health effects, social costs and technical and policy options to reduce road and rail traffic noise. *CE Delft 2007*, 64 p.

[8] Zambon, G. Benocci, R., Brambilla, G., 2016. Cluster categorization of urban roads to optimize their noise monitoring. *Environmental Monitoring and Assessment*, **188:26**, 11 p.

[9] Directive 2002/49/EC of the European Parliament and of the Council of 25 June 2002 relating to the assessment and management of environmental noise Brussels, EU/DG Environment.

[10] Vogiatzis, K., Remy, N., 2014. From environmental noise abatement to soundscape creation through strategic noise mapping in medium urban agglomerations in South Europe. *Science of the Total Environment*, **482-483**, 420 – 431.

ISBN: 978-960-6865-94-7

[11] Miguel Arana, M., García, A., 1998. A social survey on the effects of environmental noise on the residents of Pamplona, Spain. *Applied Acoustics*, **53(4)**, 245 – 253.
[12] Bastián-Monarca, N.A., Suárez, E., Arenas, J.P., 2016. Assessment of methods for simplified traffic noise mapping of small cities: Casework of the city of Valdivia, Chile. *Science of the Total Environment*, **550**, 439 – 448
[13] Ozer, S., Yilmaz, H., Yeşil, M., Yeşil, P., 2009. Evaluation of noise pollution caused by vehicles in the city of Tokat, Turkey. *Scientific Research and Essay*, **4(11)**, 1205 – 1212.
[14] Zannin, P.H.T., Diniz, F.B., Barbosa, W.A., 2002. Environmental noise pollution in the city of Curitiba, Brazil. *Applied Acoustics*, **63**, 351 – 358.
[15] Kephalopoulos, S., Paviotti, M., Anfosso-Lèdèe, F., Van Maercke, D., Shilton, S., Jones, N., 2014. Advances in the development of common noise assessment methods in Europe: The CNOSSOS-EU framework for strategic environmental noise mapping. Science of the Total Environment, **482-483**, 400 – 410.
[16] Haling, D., Cohen, H., 1996. Residential noise damage costs caused by motor vehicles. *Transportation Research Record* **1559**, 84 – 93.
[17] Houtgast, T., 1981. The effect of ambient noise on speech intelligibility in classrooms. *Applied Acoustics*, **14(1)**, 15 – 25.
[18] Brown, A.L., Chan, R., Chan, H.F., 1981. Surveying the noise exposure of classrooms. *Applied Acoustics*, **18(1)**, 55 – 67.
[19] Hygge, S., 2003. Classroom experiments on the effects of different noise sources and sound levels on long-term recall and recognition in children. *Applied Cognitive Psychology*, **17**, 895 – 914.

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Nervous toxicity of titanium dioxide nanoparticles on rat. A combined *in vivo* and *in vitro* study

C. Jun[1,2*], S. Cheng[1], L. Mei[1]

[1] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, 163 Xianlin Avenue, Nanjing 210023, Jiangsu Province, PR China
[2] Suzhou Entry-Exit Inspection & Quarantine Bureau, Suzhou 215021
*Corresponding author: Email: chen.jun.ciq@gmail.com

Abstract

Objective: To study the in vivo and in vitro toxicities of central nervous system cells in Wistar rats induced by Titanium dioxide nanoparticles (nano-TiO_2).

Methods: For in vitro study, rat astrocytes were exposed to nano-TiO_2 with three different diameters (10, 50 and 200 nm) at five concentrations (6.25, 12.5, 25, 50, 100 $mg \cdot L^{-1}$). Cellular morphology and sulfur rhodamine B (SRB) were carried out to evaluate the viability of particle-treated cells after 72 hours exposure. For in vivo study, suspensions of nano-TiO_2 with particle size of 10, 50 and 200 nm were injected into tracheas of Wistar rats at dose of 0.1, 1.0 and 10.0 $mg \cdot kg^{-1}$ in three groups, respectively. The nano-TiO_2 concentration in brain tissue and interleukin-1β (IL-1β), tumor necrosis factor-α (TNF-α), interleukin-10 (IL-10) levels in brain homogenate were detected after 72h exposure. The cell morphology of rat central nervous system induced by nano-TiO_2 was observed by light microscopy and transmission electron microscopy.

Results: Nano-TiO_2 can significantly affect the growth and morphology of rat astrocytes. The inhibition of proliferation of astrocytes was positively related to degree of nano-TiO_2 doses. With a significant dose-effect relationship, the smaller the particle size, the more obvious the inhibition effect. The nano-TiO_2 concentration and IL-1β, TNF-α, IL-10 level in rat brain tissue were increased with the concentration of nano-TiO_2 injected. The levels of these cytokines were in inverse proportion with the size of nano-TiO_2. Pathological observations indicated that the nano-TiO_2 could cause blood-brain barrier damage in rats, brain tissue necrosis. Nano-TiO_2 could enter the central nervous system cells in rats, leading to mitochondrial swelling and apoptosis. However, the non-nano-TiO_2 cannot enter the rat central nervous system. Nano-TiO_2 could inhibit the proliferation of rat glial cells and go into the rat central nervous system cells through the respiratory tract, leading to apoptosis of nerve cells. The cytotoxicity of nano-TiO_2 was dose-dependent, and in inverse proportion to particle size. The non-nano-TiO_2 showed no significant toxicity in the central nervous system cells.

Conclusions: Nano-TiO_2 may inhibit the proliferation of rat astrocytes, and enter into central nervous system cells through respiratory tracts and induce apoptosis. The titanium dioxide nanoparticles could induce dose-dependent cytotoxicity and it was inversely proportional to diameter of it. In non-nanoscale TiO_2 is avirulent. On one hand, it induces the release of IL-1β, TNF-α and other cytokines involved in inflammatory response, and damages the central nervous cells by chemotaxised activated inflammatory cells; on the other hand, it induces apoptosis of central nervous system cells.

Keywords: titanium dioxide; rat toxicity; nervous system; nanoparticles

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1. INTRODUCTION

Nanosize titanium dioxide (nano-TiO_2) materials, for their peculiar physicochemical properties, are widely applied in consumer products, food additives, cosmetics, drug carriers, and so on[1-2]. Under these circumstances, an assessment of risk and appropriate safety measures based on the available limited data for nanomaterials characterization and safety protocols are needed to protect human health and the environment. Due to unique properties, nano-TiO_2 exposed to the tissues or fluids would immediately adsorb macromolecules they encounter, thereby affecting the regulating mechanisms of enzymes or other proteins, resulting in loss of activity of a number of hormones or enzymes in the body [3-4]. It has been noted that nanoparticles may lead to the possibility of adverse biological effects, and the behavior of nanoparticles on the target organ depends largely on their size, shape and interactions with the surrounding tissue [5-8]. This increased human and environmental exposure to TiO_2 nanoparticles has led to an intense scrutiny of its biocompatibility resulting in many animal and in vitro studies that suggests a need for concern.

As exogenous substances, nano-TiO2 demonstrates a high degree of mobility after intentionally injected (implanted) into the body by inhalation, swallowing, skin absorption or in the medical process [9]. Once nano-TiO2 particles are in the body, they may be redistributed into other tissues (such as the liver, heart, lung, etc.), which could induce impairments on organs after unintentional exposure. Although exposure to different nano-TiO2 particle sizes and formulations has produced only marginal results in rodents[10-11], Previous *in vitro* studies indicated that TiO2 nanoparticles could cause oxidative stress (OS)-mediated toxicity in diverse cell types, including human colon cells[12], osteoblasts [13], endothelia [14], epithelia [15], skin fibroblast [16], liver [17], and alveolar macrophages[18]. Several studies have suggested that inhaled or injected nanoparticles enter systemic circulation [19] and migrate to various organs and tissues, raising concern that they may cause damage to biological systems through OS pathways [20]. The brain is especially vulnerable to OS damage, and recent studies indicate that nanosize particles can cross the blood-brain barrier [21] and enter the central nervous system (CNS) of animals [22]. There has been some argument about whether or not nano-TiO_2 can cross the blood-brain barrier, which separates blood from cerebrospinal fluid and is made of endothelial cells connected by tight junctions that limit the entry of many substances into the brain. Several studies have indicated direct disruption of neuronal cell membranes by nano-TiO_2 would allow their entry into the brain [23,24], and significant nano-TiO_2 accumulation in the brain while cellular toxicity assessment demonstrate negative effects on neuronal cell viability and function[25-27]. Intranasal exposure of TiO_2 nanoparticles also demonstrated high accumulation of the nanoparticles in different regions of the brain resulting in increase of glial fibrillary acidic protein (GFAP) positive cells, oxidative stress, and brain tissue damage [28]. As the nasal cavity and the olfactory bulb are connected through the olfactory neural pathway, this particular structure provides a favorable condition for the exogenous inhaled nanoparticles directly into the central nervous system along the olfactory nerve pathway other than the blood-brain barrier [29].

Studies have shown that nanoparticle transport was exclusively transcellular. Nanoparticles can enter olfactory bulb through the olfactory nerve of experimental animals and migrate to the brain, causing increased mRNA levels of macrophage inflammatory protein, glial fibrillary acidic protein and neural cell adhesion molecule in central nervous system [30-31]. The processes of translocation of nano-TiO_2 into the brain would be regulated by several parameters, such as administration routes, size, and surface modification. However, Current knowledge about neurotoxicity induced by nano-TiO_2 is insufficient and more detailed and standardized researches are needed [32-34]. Little information is available regarding factors such as surface characteristics and size that may affect the transport of nanoparticles from the nasal cavity to the central nervous system. In this paper, we try to clarify the mechanism of toxic effects of nano-titanium dioxide on the rat CNS cells through in vitro and in vivo experiments. We utilized three different diameters of nano-TiO2 particles (10, 50

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and 200 nm) in vivo and in vitro to probe the mechanism the cytotoxicity nano-TiO2 exerts on rat neuroglia cells initially. Our findings provide compelling evidence that TiO2 nanoparticle exposure has potential implications in astrocyte-mediated neurological dysfunction.

2. MATERIALS AND METHODS

Materials

Nanosized TiO_2 powder materials (10nm, 30nm, 200nm) were obtained, as uncoated nanoparticles, from Nanjing University. The nano-TiO_2 stock solutions were made at a stock concentration of 1.0 $g \cdot L^{-1}$ in minimum essential medium (MEM) and diluted to final concentrations varying from 6.25–100 $mg \cdot L^{-1}$. Normal rat astrocytes CTX TNA2 was purchased from ATCC (MA) and culture medium were purchased from ScienCell Research Laboratories, Inc. (Carlsbad, CA). The cells were cultured in astrocyte medium, maintained at 37℃ in a humidified incubator containing 5% CO_2. 96-well culture plates (Nature Gene Corp., USA) and MEM culture medium (Gibco) were used for cell culture. Rat IL-1β, TNF-α, IL-10 Elisa Kit were purchased from Rapidbio Corp., USA. A total of 30 male Wistar rats, with the weight of 250 ~ 300g, purchased from Laboratory Animal Center of Soochow University, were randomly divided into four groups: control group (intratracheal instillation of sterile saline); low-dose group ($0.1 mg \cdot kg^{-1}$); moderate-dose group ($1 mg \cdot kg^{-1}$); high-dose group ($10 mg \cdot kg^{-1}$). Stock titanium standard solution (1000 $\mu g \cdot mL^{-1}$) for ICP-MS was purchased from Fisher Scientific (Leicestershire, UK). Calibration standards for ICP-MS analysis were prepared within a range from 0 to 500 $\mu g \cdot L^{-1}$ from the stock Ti solution in 5% HNO_3. Pentobarbital of 2% was intraperitoneal injected into anesthetized rats by 30mg·kg-1, and intratracheal instillation was performed with nanoparticles suspension [35].

Characterization of NPs

For preparation of exposure medium, nano-TiO_2 materials were weighed in polypropylene tubes and dispersed in deionized water. To achieve maximum dispersion, the suspension was homogenized using vortex (Daigger Vortex-Genie 2, Model G560) equipped with a titanium probe. The characterizations of the nano-TiO_2 suspension were performed using Transmission electron microscopy (TEM) and Dynamic light scattering (DLS) techniques. Size measurements in dried suspension were made by TEM, while DLS provided the size distribution for the hydrated forms of the nano-TiO_2 particles. For TiO_2 nanoparticle suspension solution, the TEM images revealed that the particles are present as aggregates, leading to stable suspensions with much higher hydrodynamic diameters(Figure 1). Nano-TiO_2 particles are highly hydrophobic; therefore they aggregate substantially in aqueous solutions. The stability and aggregation behaviors of nanoparticles within aquatic media are determined by DLS (Figure 2). Nevertheless, for all three suspensions, the TEM images indicate that not exclusively aggregated but also single particles were present. Such conditions are characteristic of cell culture studies and may produce higher particle exposures while the higher sedimentation rate seen at higher concentrations could be consistent with larger sized aggregates formed at the higher test concentrations of TiO_2 nanoparticles.

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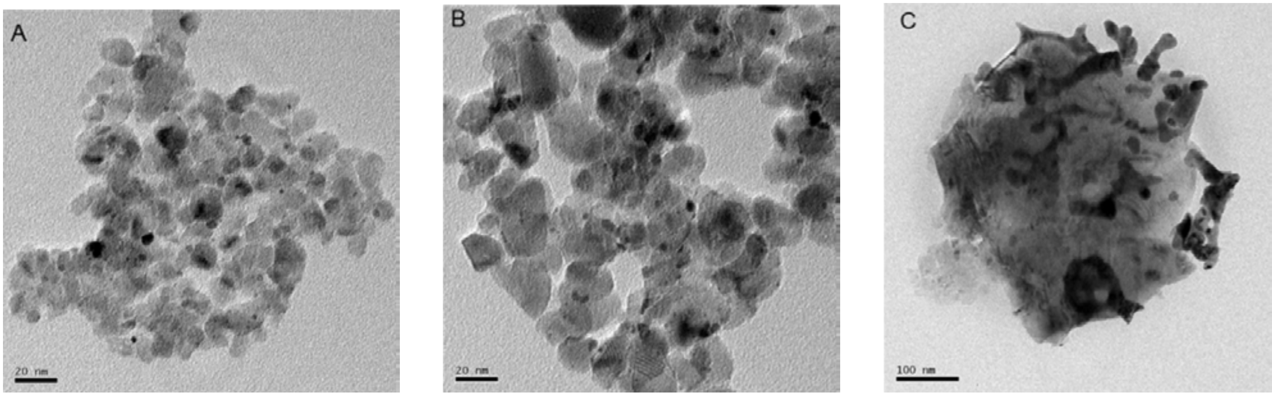


Figure 1Q Suspension of titanium dioxide nanoparticles (nano-TiO2) observed by electron microscope (x10 000).
(A) 10 nm diameter particles, (B) 50 nm diameter particles
and (C) 200 nm diameter particles. There is a ruler in the Figure.

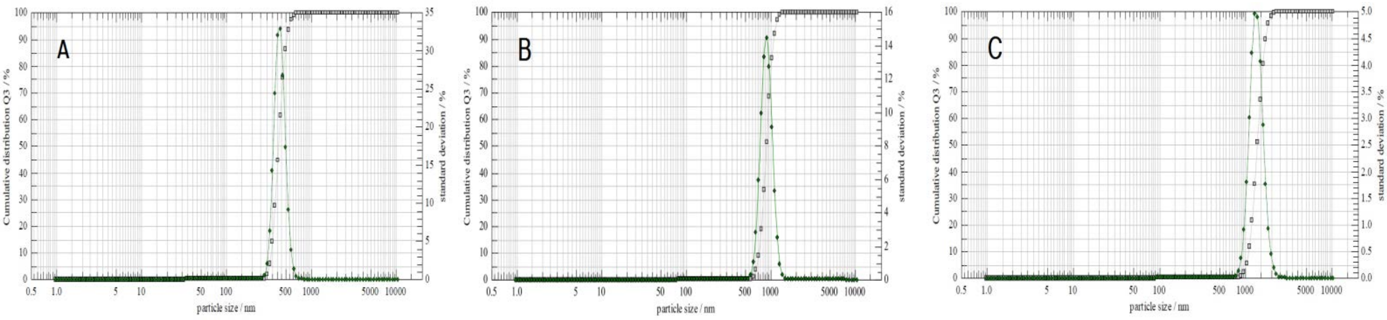


Figure 2. DLS analysis showing a size distribution (PSD) of hydrodynamic TiO_2 nanoparticles at the concentration of 1.0 mg·L^{-1}
(A) 10 nm nano-TiO2 solution, (B) 50 nm nano-TiO2 solution
and (C) 200 nm nano-TiO2 solution.

Cell viability assay in vitro

The cells cultured for 24 hours were digested with the pancreatin of 0.25%; they were then blown and beaten to be a unicellular suspension; the density of the suspension was adjusted to 8×107L_1. One hundred microlitres of the suspension was seeded onto each well of the polylysinecoated 96-well plates. Four wells are set for each group. Cells have been found 60% adherent under inverted microscope after 24h culture, nano-particle suspension with various concentrations (6.25, 12.5, 25, 50, 100 mg·L^{-1}) were added slowly in the 96-well plates. Then, the 96-well plates were cultured at 37℃ in a humidified incubator containing 5% CO_2 for 72 hours. Cell viability assay was evaluated by Sulforhodamine B staining assays. The percentage of viable cells was used to evaluate the rat astrocyte activity affected by nano-titanium dioxide, the calculation formula is shown as follows:

$$Percentage\ of\ \ viable = \frac{OD\ value\ of\ \ exposed\ cells}{OD\ value\ of\ \ control\ cells}$$

The curve was fitted with the concentration of nano-titanium dioxide as x-coordinate and the percentage of cell viability as y-coordinate.

Toxicity of nano-TiO_2 on rats in vivo

Nano-TiO_2 exposure was conducted to assess astrocyte-mediated neurological dysfunction on Wistar rats by exposing the rats to three different doses, 0.1, 1.0 and 10.0 mg·kg^{-1}, using intratracheal instillation. Thirty homogenous Wistar male rats (250~300g) were randomly divided

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into four groups with three test groups including nine rats and a control group including three rats. The test animals were arranged into three test groups on the basis of the nano-TiO_2 dosages with each group distributed equally into three sub-groups according to nanoparticle diameters. Before intratracheal instillation, the rats were kept in a fasting condition and then anesthetized with 2% pentobarbital of 30 mg kg^{-1} for 15 minutes. The trachea administration was implemented to the rats under supine head-up conditions by means of intratracheal instillation at a instillation speed of 40ml/min. Meanwhile, the control group was administered with stroke-physiological saline solution. Seventy-two hours after treatment, all rats were sacrificed to detect the nano-TiO_2 content by ICP-MS after a microwave assisted digestion with a HNO_3/H_2O_2 mixture, and currently measure the cytokine production (IL-1β, IL-10, and TNF-α) in rat brain tissue by radioimmunoassay. The pathological damnification of nano-TiO2 on the cortex of rat brain tissues was observed by HE staining.

Statistics

All data were collected using SAS 8.0 software (SAS Institute, Cary, NC) . Graphing and statistics were performed with Excel 2015 (Microsoft, Redmond, WA). The mean value at each concentration was graphed to show a time-course response. At least five time points are depicted for each assay. The quantitative variables were analyzed by ANOVA. Dunnett t was used to analyze the groups. SNK method was applied to compare one group with another. The exposure concentration/time point at which a statistically significant difference was observed is indicated on the graphs (*, $p<0.05$) and described in the figure legends.

3. RESULTS

Cytotoxicity of normal rat astrocytes by nano-TiO_2

Nano-TiO_2 can significantly affect the growth and morphology of rat astrocytes with a significantly dose-effect relationship between inhibition of astrocyte proliferation and nano-TiO_2 doses. During the exposure times described in the TEM studies, the rat neuroglia cells(which adhere to the bottom of the cell culture plate/well), were exposed by particle diffusion or sedimentation of aggregates. After the rat neuroglia cells were exposed to 50 and 100 $mg·L^{-1}$ nano-TiO_2 suspension solution with the different diameters (10 and 50 nm and 200nm) for 24 hours in vitro, the cells have been found 60% adherent under inverted microscope after 24h culture (Figure 3a). After 72 hours exposure, the cell survival rate was decreased with increasing Nano-TiO_2 concentration (Fig 3b). Meanwhile, obvious changes happened, such as rebound and transmogrification to the different extent, increasing cell spaces, sparse arrangement and decreasing cellular transparency, especially at the concentration of 100 $mg·L^{-1}$. The results also indicated that the nano-TiO_2 with smaller diameter of 10nm and 50nm had more obvious inhibition effect on the activity of cells, while the concentrations of nano-TiO_2 with the diameter of 200 nm have no significant effects on cellular morphology.

Bioaccumulation of nano-TiO_2 content in rat brain tissue

The nano-TiO_2 content showed statistically significant difference among the middle, the high dose and the control group. Only the nano-TiO_2 content of high-dose group had increased significantly (10nm, 363.82%; 50nm, 669.69%), the nano-TiO_2 with diameter of 200 nm in brain tissue did not change significantly (Figure 4).

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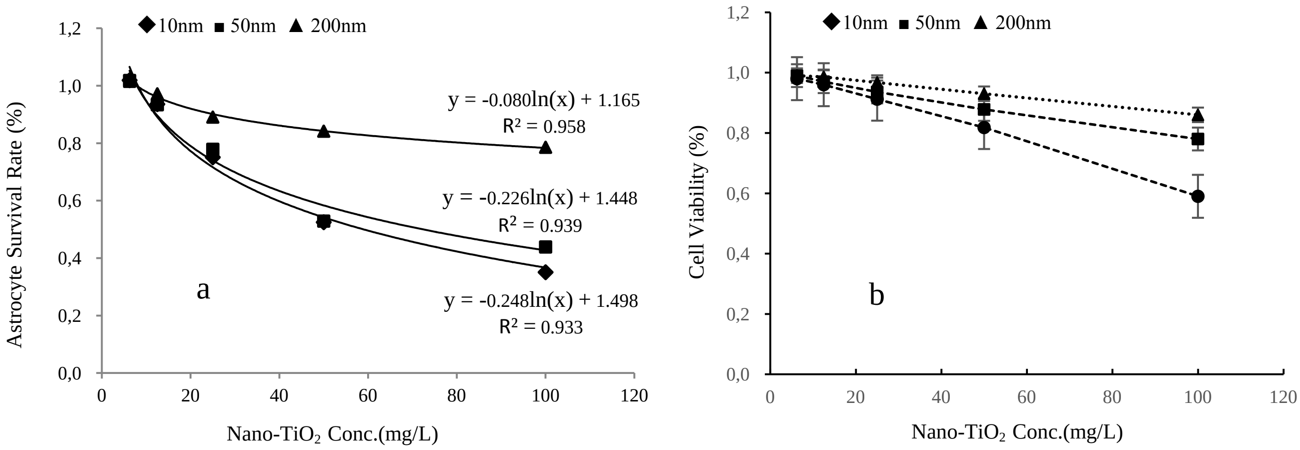


Figure 3(a,b). The activity of Nano-TiO_2 treated rat astrocyte detected by SRB assay

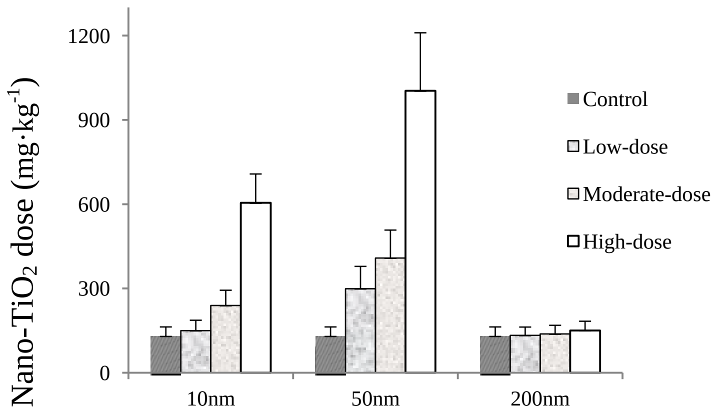


Figure 4. The nano-TiO_2 content in rat brain tissue. high-dose group compared with control group, *P<0.05

Morphology changes of normal rat astrocytes by nano-TiO_2

With the increase of nano-particle concentration of 10 nm and 50 nm diameter, adherent cells decreased significantly and showed intracellelur phagocytic particles (Fig 5a, 5b). Nano-TiO_2 with diameter 200nm at three different volumes (0.1, 1.0 and 10.0 mg kg^{-1}) had no obvious effect on cell morphology (Fig 5c). no nanometer particles were seen in cells through a transmission electron microscope

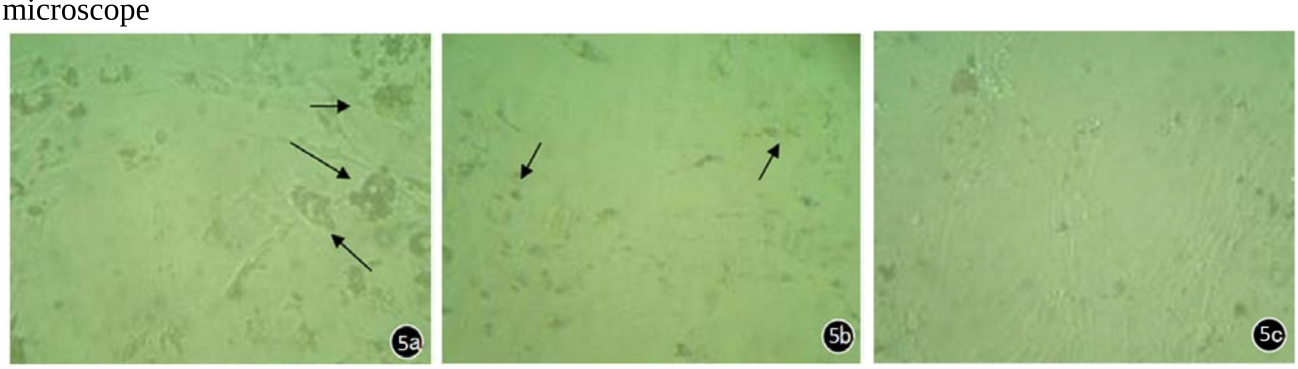


Figure 5. Microscope photos of rat glial cells exposed to nano-TiO_2 with diameter of 10, 50, 200 nm for 72h

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In agreement with earlier findings, exposure to nano-TiO_2 particles caused cell shrinkage plus irregular membrane borders compared with the control cells. Microscopy revealed that TiO_2 nanoparticles and agglomerates were effectively internalized by rat neuroglia cells. After the rat neuroglia cells were exposed to nano-TiO2 of two different diameters (10 and 50 nm) at the concentrations of 1.0 mg kg^{-1}, Transmission electron microscope showed intracellular edema around the nucleus of rat glial, mitochondrial swelling, entrance of nano-TiO_2 into the cytoplasm, and apoptosis. the higher the doses of nano-TiO_2, the higher the extent of injuries of brain tissues (Figure 6).

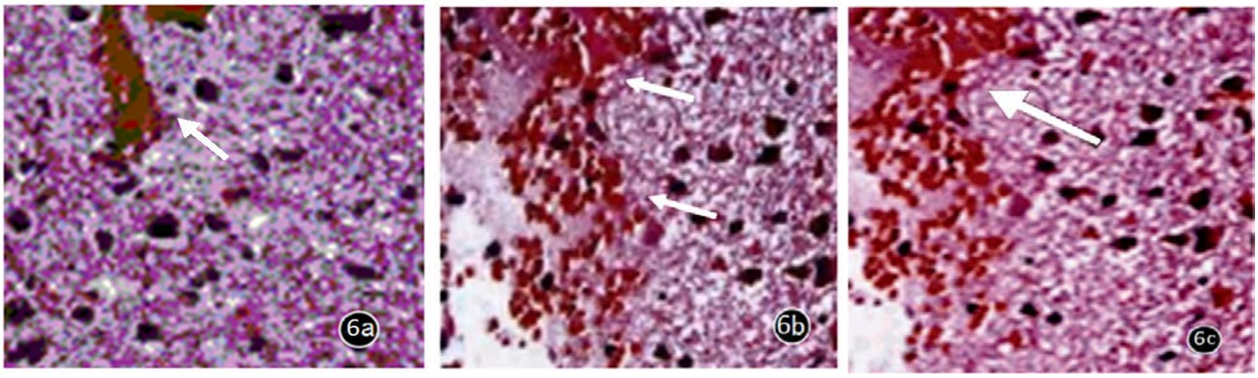


Figure 6. Pathological observations of rat brain tissue by different doses of nano-TiO_2 exposure for 72h (HE stained sections under light microscope ×400) A: middle-dose group; B: high-dose group.

These effects were positively related to the dose and negatively related the size of nano-TiO_2 (Figure 7b, c, d, e, h). The brain tissue of 200nm group had no these changes.

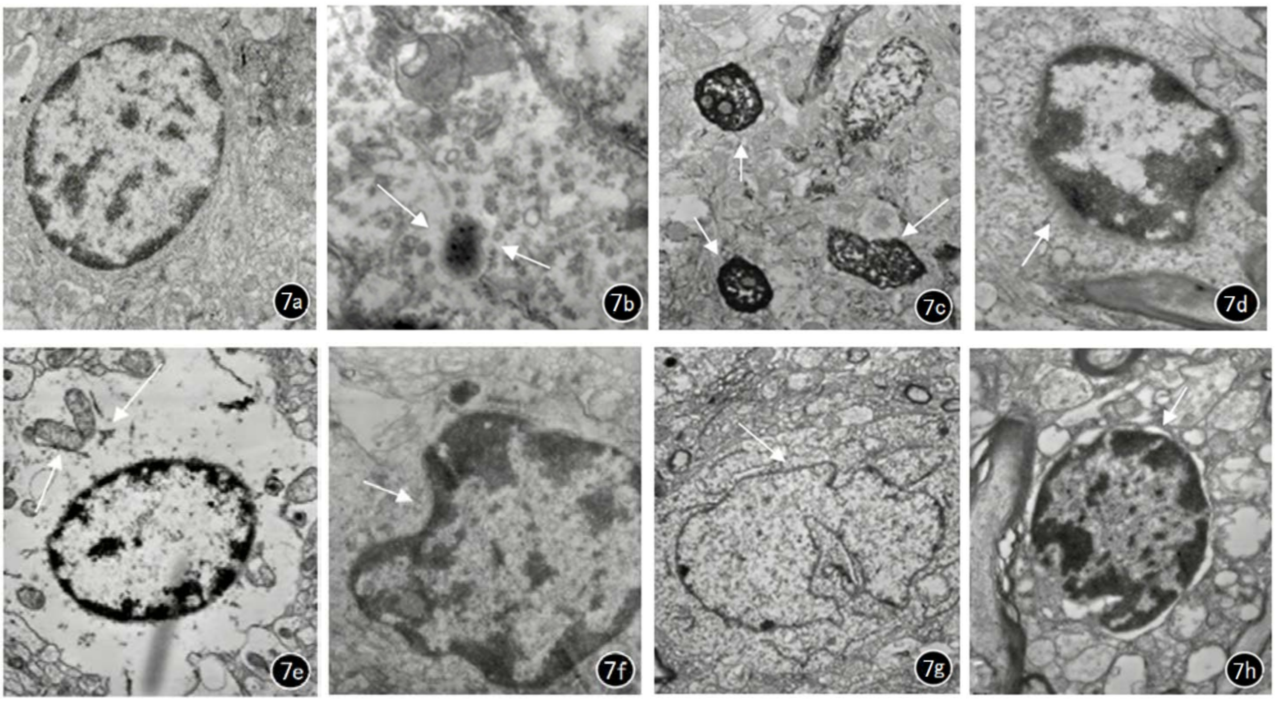
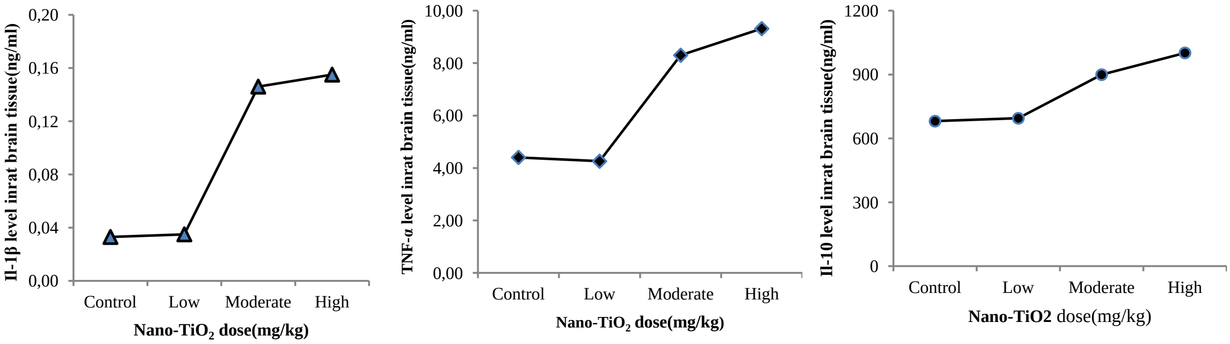


Figure 7: Pathological observations of rat brain tissue by different doses of nano-TiO2 exposure for 72h (under transmission electron microscope ×15000) A: normal group; B: 10nm group (10mg/kg), seen cytoplasmic nanoparticles (arrows) C: 10nm group (10mg/kg), nano-particles are swallowed into the cytoplasm glial cells and aggregated into groups (arrows); D: 10nm group (1mg/kg), apoptosis, cell shrinkage, chromatin margination are obvious (arrows) E: 50nm group (10mg/kg), nuclear edema, mitochondrial swelling, reduced number of ribosomes, chromatin margination and nucleolar irregularity; F,G: 50nm group (1mg/kg), deformed nucleus changes; H: 20nm group (10mg/kg), cell shrinkage, chromatin margination and apoptotic.

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The cytokine levels in rat brain tissue by nano-TiO_2

In the group of 10nm and 50nm diameter, the activity of IL-1β, TNF-α, IL-10 was positively proportional to the concentration of nano-TiO_2, the higher the concentration, the higher the activity of these cytokines(Fig 8). The activity of cytokines was inversely proportional to the diameter of nano-TiO_2, the smaller the diameter, the higher activity of cytokines. The nano-TiO_2 with diameter of 200nm had no obvious effect on IL-1β, TNF-α and IL-10 activity in rat brain tissue.



Figiure 8: Cytokine levels in rats brain tissue exposed to 10nm nano-TiO_2

4. DISCUSSION

Numerous *in vivo* researches adopted rats or mice for the experimental models, and they were exposed to nano-TiO_2 for bio-safety assessment. Small-sized particles have better mobility and it is expected that the transportation of nanoparticles across the BBB is possible either by passive diffusion or by carrier-mediated endocytosis[36]. In addition, nanoparticles may be taken up directly into the brain by trans-synaptic transport[37]. It has also been reported that nanoparticle exposure can induce impairments to normal neurons[38], microglia[39]and even aggravate the process of brain pathology[40]. In this study, through tracheal instillation of nano-particle suspension, we found that nano-TiO_2 can enter the cytoplasm of rat central nervous system cells (Figure 7b, c). This indicated that nano-TiO_2 can enter the central nervous system through respiratory tract. Although *some previous studies have shown* that there was no significant correlation between the toxicity of nano-TiO2 and its diameter and surface area[41], our study found that the nanoscale (<100nm) of titanium dioxide have changed its physical and chemical properties, and their toxicity was related to and their diameters.

Nano-TiO_2 can significantly affect the growth and morphology of rat astrocytes. Under transmission electron microscope, the nano-particles can be seen to enter the rat central nervous system cells and lead to apoptosis. This is due to the following reasons: Nano-TiO_2 are free to enter the pulmonary capillaries through the alveolar epithelium and enter the brain tissue through circulation; Nano-TiO_2 can damage the blood-brain barrier and enter the central nervous system cells, resulting in apoptosis; Unlike Nano-TiO_2, non-nano-scale-TiO_2 (>100nm) cannot freely go through the blood-brain barrier, and have no significant toxicity on rat central nervous system cells.

Once the nano-TiO_2 were transported into the brain regions, major cells in the CNS, including the neurons and the glial cells, would be affected. Our research demonstrated that there were obvious changes in the cellular configuration in rat astrocytes when nano-TiO_2-treated, such as cellular contraction, increscent cell spaces, increased intracellular particles and decreasing cellular transparency. Among them, the nano-TiO_2 of two different diameters (10 and 50 nm) affected the cells significantly. This research discovered the nano-TiO_2 of two different partied diameters (10 and 20 nm) could cause the dosage dependent pathological damages of rat brain tissue, one of

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which was mainly inducing the inflammatory reaction. The nano-TiO_2 with the particle diameter of 200 nm didn't bring about any obvious pathological changes.

The inflammatory cell factors IL-1β, TNF-α and IL-1 had a close relation with cerebral injury. The current assumption is that, after cerebral injury, the IL-1β and TNF-α in brain tissue would increase in content. This research revealed that, for the nano-TiO_2 of two different particle diameters (10 and 50 nm), nano-TiO_2, IL-1β, TNF-α and IL-10 in rat brain tissue were all increased in level, with the increasing of the nano-TiO_2 dosage, the pathological damage in rat brain tissue became more serious and there were no significant changes for the nano-TiO_2 with the particle diameter of 200 nm.

Above selection of findings on nanoparticle toxicity on the central nervous system can be illustrated to elucidate these points, can exert cytotoxicity on the rat brain neuroglia cells, with its toxicity being related to the particle diameter of nano-TiO2 and its mechanism being concerned with the inducing inflammatory reaction. Based on the results achieved upon the method comparison conducted using a homogeneous dispersion of nanoparticles, there remains further study to collect data on the behavior of trans-synaptic transport and neurotoxicity signs symptoms of neurotoxicity syndromes of nano-TiO2 in the central nervous systems under simulated conditions focused on daily exposure routine.

5. CONCLUSION

This study showed the nano-TiO_2 holding the particle diameter within a certain length range instilled into the lung could permeate the blood–brain barrier to enter the rat brain tissue so as to induce the inflammatory reaction, thus posing the dosage-dependent damage to the rat brain neuroglia cells. Nano-TiO2 can exert cytotoxicity on the rat brain neuroglia cells, with its toxicity being related to the particle diameter of nano-TiO2 and its mechanism being concerned with the inducing inflammatory reaction. The inhibition of proliferation of astrocytes was positively related to degree of nano-TiO_2 doses. With a significant dose-effect relationship, the smaller the particle size, the more obvious the inhibition effect. The nano-TiO_2 concentration and IL-1β, TNF-α, IL-10 level in rat brain tissue were increased with the concentration of nano-TiO_2 injected. The levels of these cytokines were in inverse proportion with the size of nano-TiO_2. Pathological observations indicated that the nano-TiO_2 could cause blood-brain barrier damage in rats, brain tissue necrosis. Nano-TiO_2 could enter the central nervous system cells in rats, leading to mitochondrial swelling and apoptosis. However, the non-nano-TiO_2 cannot enter the rat central nervous system. Nano-TiO_2 could inhibit the proliferation of rat glial cells and go into the rat central nervous system cells through the respiratory tract, leading to apoptosis of nerve cells. The cytotoxicity of nano-TiO_2 was dose-dependent, and in inverse proportion to particle size. The non-nano-TiO_2 showed no significant toxicity in the central nervous system cells.

References

[1] W J Stark, P R Stoessel, W Wohlleben, A Hafner. Industrial applications of nanoparticles[J]. Chem. Soc. Rev., 2015, 44(16): 5793–5805

[2] Fabiano Piccinno, Fadri Gottschalk, Stefan Seeger, Bernd Nowack. Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world[J]. J. Nanopart. Res., 2012, 14:1109–1120

[3] S Austin Hammond, Amanda C Carew, Caren C. Helbing. Evaluation of the Effects of Titanium Dioxide Nanoparticles on Cultured Rana Catesbeiana Tailfin Tissue[J]. Front Genet. 2013, 4: 251

[4] Hongbo Ma, Stephen A Diamond. Phototoxicity of TiO2 nanoparticles to zebrafish (Danio rerio) is dependent on life stage[J]. Environmental Toxicology and Chemistry, 2014, 32(9): 2139–2143

[5] Tiezheng Tong, Carolyn M Wilke, Jinsong Wu, Chu Thi Thanh Binh, John J Kelly, Jean-François Gaillard, Kimberly A Gray. Combined Toxicity of Nano-ZnO and Nano-TiO2: From Single to Multinanomaterial Systems[J]. Environ. Sci. Technol., 2015, 49 (13): 8113–8123

ISBN: 978-960-6865-94-7

[6] Senlin Lu, Wenchao Zhang, Rui Zhang, Pinwei Liu, Qiangxiang Wang, Yu Shang, Minghong Wu, Ken Donaldson, Qingyue Wang. Comparison of Cellular Toxicity Caused by Ambient Ultrafine Particles and Engineered Metal Oxide Nanoparticles[J]. Particle and Fibre Toxicology, 2015, 12:5
[7] Oberdörster G, Oberdörster E, Oberdörster J. Nanotoxicology: An Emerging Ddiscipline Evolving from Studies of Ultrafine Particles[J]. Environ Health Perspect. 2009; 113(7):823–39
[8] Jiangxue Wang, Ying Liu, Fang Jiao, Fang Lao, Wei Li, Yiqun Gu, Yufeng Li, Cuicui Ge, Guoqiang Zhou, Bai Li, Yuliang Zhao, Zhifang Chai, Chunying Chen. Time-dependent Translocation and Potential Impairment on Central Nervous System by Intranasally Instilled TiO_2 Nanoparticles[J]. Toxicology, 2008, 254(1-2): 82–90
[9] Andreas Elsaesser, C Vyvyan Howard. Toxicology of nanoparticles[J]. Advanced Drug Delivery Reviews2012, 64(2): 129–137
[10] Bermudez E., Mangum J B, Wong B A, Asgharian B, Hext P M, Warheit D B, Everitt J I. Pulmonary responses of mice, rats, and hamsters to subchronic inhalation of ultrafine titanium dioxide particles[J]. Toxicol. Sci. 2004, 77: 347–357
[11] Warheit D B, Brock W J, Lee K P, Webb T R, Reed K L. Comparative pulmonary toxicity inhalation and instillation studies with different TiO_2 particle formulations: impact of surface treatments on particle toxicity[J]. Toxicol. Sci. 2005, 88: 514–524
[12] Zhang A P, Sun Y P. Photocatalytic killing effect of TiO_2 nanoparticles on Ls-174-t human colon carcinoma cells[J]. World J. Gastroenterol. 2004, 10: 3191–3193
[13] Ramires P A, Romito A, Cosentino F, Milella E. The influence of titania/hydroxyapatite composite coatings on in vitro osteoblasts behaviour[J]. Biomaterials 2001, 22: 1467–1474
[14] Peters K, Unger R E, Kirkpatrick C J, Gatti A M, Monari, E. Effects of nanoscaled particles on endothelial cell function in vitro: studies on viability, proliferation and inflammation[J]. J Mater. Sci. Mater. Med. 2004, 15: 321–325
[15] Gurr J-R, Wang A S, Chen C-H, Jan K-Y. Ultrafine titanium dioxide particles in the absence of photoactivation can induce oxidativedamagetohumanbronchial epithelial cells[J]. Toxicology 2005, 213, 66–73
[16] Wamer, W G, Yin J J, Wei R R. Oxidative damage to nucleic acids photosensitized by titanium dioxide[J]. Free Radical Biol.Med. 1997, 23: 851–858.
[17] Hussain S M, Hess K L, Gearhart J M, Geiss K T, Schlager J J. In vitro toxicity of nanoparticles in BRL 3A rat liver cells[J]. Toxicol. In Vitro 2005, 19: 975–983
[18] Renwick L C, Donaldson K, Clouter A. Impairment of alveolar macrophage phagocytosis by ultrafine particles[J]. Toxicol. Appl. Pharmacol. 2001, 172: 119–127
[19] Meiring J J, Borm P J, Bagate K, Semmler M, Seitz J. Takenaka S, Kreyling W G. The influence of hydrogen peroxide and histamine on lung permeability and translocation of iridium nanoparticles in the isolated perfused rat lung[J]. Part. Fibre Toxicol. 2005: 2–3
[20] Samet J M, DeMarini D W, Malling H V. Doairborne particles induce heritable mutations? Science 2004, 304: 971-972
[21] Lockman P, Oyewumi M, Koziara J, Roder K, Mumper R, Allen D. Brain uptake of thiamine-coated nanoparticles[J]. J. Controlled Release 2003, 93: 271–282.
[22] Oberdörster G, Sharp Z, Atudorei V, Elder A, Gelein R, Kreyling W, Cox C. Translocation of inhaled ultrafine particles to the brain[J]. Inhal. Toxicol. 2004, 16: 437–445
[23] Sharma, H S, Sharma, A. Nanoparticles aggravate heat stress induced cognitive deficits, blood-brain barrier disruption, edema formation and brain pathology[J]. Prog. Brain Res. 2007, 162: 245–273.
[24] Sharma H S, Sharma A. Conference scene: Nanoneuroprotection and nanoneurotoxicity: Recent progress and future perspectives[J]. Nanomedicine 2010, 5, 533–537.
[25] Frans M Christensen, Helinor J Johnston, Vicki Stone, Robert J. Aitken, Steve Hankin, Sheona Peters, Karin Aschberger. Nano-TiO_2-feasibility and challenges for human health risk assessment based on open literature[J]. Nanotoxicology, 2011, 5(2): 110–124
[26] Marcos E Bruno, Maximiliano Sittner, Rómulo L Cabrini, María B Guglielmotti, Daniel G. Olmedo, Deborah R. Tasat. In vitro age dependent response of macrophages to micro and nano titanium dioxide particles[J]. Journal of Biomedical Materials Research Part A, 2015, 103(2): 471–478
[27] Stefaan J Soenen, Wolfgang J Parak, Joanna Rejman, Bella Manshian. Cellular Stability of Inorganic Nanoparticles: Effects on Cytotoxicity, Particle Functionality, and Biomedical Applications[J]. Chem. Rev., 2015,115(5): 2109–2135
[28] Jiangxue Wang, Chunying Chen, Ying Liu, Fang Jiao, Wei Li, Fang Lao, Yufeng Li, Bai Li, Cuicui Ge, Guoqiang Zhou, Yuxi Gao, Yuliang Zhao, Zhifang Chai. Potential Neurological Lesion after Nasal Instillation of TiO_2 Nanoparticles in the Anatase and Rutile Crystal Phases[J]. Toxicology Letters, 2008, 183(1-3): 72–80
[29] Alpesh Mistry, Snjezana Stolnik, Lisbeth Illum. Nose-to-Brain Delivery: Investigation of the Transport of Nanoparticles with Different Surface Characteristics and Sizes in Excised Porcine Olfactory Epithelium[J]. Mol. Pharmaceutics, 2015, 12(8): 2755–2766

ISBN: 978-960-6865-94-7

[30] Guilherme J M Garciaab, Jeffry D Schroeterc, Julia S Kimbelld. Olfactory deposition of inhaled nanoparticles in humans[J]. Inhalation Toxicology: International Forum for Respiratory Research, 2015, 27(8): 394–403
[31] Sandra Gissela Márquez-Ramírez, Norma Laura Delgado-Buenrostro, Yolanda Irasema Chirino, Gisela Gutiérrez Iglesias, Rebeca López-Marure. Titanium Dioxide Nanoparticles Inhibit Proliferation and Induce Morphological Changes and Apoptosis in Glial Cells[J]. Toxicology, 2012, (3-2): 146–156
[32] Yuguan Ze, Lei Sheng, Xiaoyang Zhao, Xiao Ze, Xuecen Wang, Qiuping Zhou, Jialiang Liu, Yifei Yuan, Suxin Gui, Xuezi Sang, Qingqing Suna, Jie Hong, Xiaohong Yu, Ling Wang, Bingyan Li, Fashui Hong. Neurotoxic Characteristics of Spatial Recognition Damage of the Hippocampus in Mmice Following Subchronic Peroral Exposure to TiO_2 Nanoparticles[J]. Journal of Hazardous Materials, 2014, 264(15): 219–229
[33] Magdalena Czajka, Krzysztof Sawicki, Katarzyna Sikorska, Sylwia Popeka, Marcin Kruszewski, Lucyna Kapka-Skrzypczak. Toxicity of Titanium Dioxide Nanoparticles in Central Nervous System[J]. Toxicology in Vitro, 2015, 29(5): 1042-1052
[34] Tin-Tin Win-Shwe, Hidekazu Fujimaki. Nanoparticles and Neurotoxicity[J]. Int. J. Mol. Sci. 2011, 12(9): 6267-6280
[35] Yasuko Hasegawa-Baba, Hisayo Kubota, Ayako Takata, Muneyuki Miyagawa. Intratracheal Instillation Methods and the Distribution of Administered Material in the Lung of the Rat[J]. J. Toxicol. Pathol., 2014, 27(3–4): 197–204.
[36] Günter Oberdörster, Andrew Maynard, Ken Donaldson, Vincent Castranova, Julie Fitzpatrick,*et al*. Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy[J]. Particle and Fibre Toxicology2005, 2:8
[37] Oberdörster G, Sharp Z, Atudorei V, Elder A, Gelein R, Kreyling W, Cox C. Translocation of inhaled ultrafine particles to the brain[J]. Inhal Toxicol. 2004, 16(6-7): 437-45.
[38] Tang M, Xing T, Zeng J, Wang H, Li C, Yin S, Yan D, Deng H, Liu J, Wang M, Chen J, Ruan D Y.. Unmodified CdSe quantum dots induce elevation of cytoplasmic calcium levels and impairment of functional properties of sodium channels in rat primary cultured hippocampal neurons[J]. Environ. Health Perspect. 2008, 116(7): 915–922.
[39] Au C, Mutkus L, Dobson A, Riffle J, Lalli J & Aschner M. Effects of nanoparticles on the adhesion andcell viability on astrocytes[J]. Biol. Trace Elem. Res. 2007, 120, 248–256
[40] Sharma, H. S. & Sharma, A. Nanoparticles aggravate heat stress induced cognitive deficits, blood-brain barrier disruption, edema formation and brain pathology[J]. Prog. Brain Res. 2007, 162, 245–273.
[41] David B Warheit, Thomas R Webb, Christie M Sayes, Vicki L Colvin, Kenneth L Reed. Pulmonary Instillation Studies with Nanoscale TiO_2 Rods and Dots in Rats: Toxicity Is not Dependent upon Particle Size and Surface Area[J]. Toxicological Science, 2006, 91(1): 227–236

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Environmental Economics

PROTECTION
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XIII

Who's to blame for Greece?
Austerity in charge of saving a broken economy.
Paying the price of the political risk

T. Pelagidis[1*], M. Mitsopoulos[2]

[1] Brookings Institution, Washington DC, USA - University of Piraeus, 21 Lambraki Ave., Piraeus 185 33, Greece
[2] Boston University, Hellenic Federation of Enterprises, Xenophontos 5, 10557, Greece
*Corresponding author: Email: pelagidi@unipi.gr

Abstract

An assessment of the dynamics and importance of Greece's potential Grexit is made to point out its pivotal role during the Eurozone's current crisis. Subsequently the case of the independence movement of Quebec is examined, to argue that once perceptions about the separation from a Union –such as Greece's Grexit- take root they may propagate themselves for long periods of time entrenching an uncertainty that leads to concrete economic damage. Therefore the need to accelerate "convergence in institutions" among the Union members is highlighted, as is the need to acknowledge that political developments in Greece are in line with the predictions of a growing literature on the causes and impact of political risks.

Keywords: Greek economy; domestic politics, IMF, economic crisis, austerity

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1. INTRODUCTION

The relationship between stringent regulation and economic activity has been linked in the literature with the development of beliefs and therefore political dynamics that turn these beliefs into politics. For example, the tight regulation of markets and ineffectiveness of the judiciary has been linked with such trust by Agnion et al. (2008). As a matter of fact in the presence of high regulation of entry and activity, investment in social capital may not be effective, as when citizens know that within a setting of high regulation and corruption their investment will not lead to satisfactory yields, they will eschew such investment and opt for free-riding and corruption. In such cases citizens ask for even more regulation, to curb the negatively perceived corporate activity, as argued by di Tella and McCullock (2007). Thus, a path is taken, along which high regulation by the government leads to economic inefficiencies that lower growth and prosperity while increasing corruption. This setting increases political demand for even more regulations that further harm economic activity and cement political beliefs that are hostile to a free trade and free market economy. Though this mechanism di Tella and McCullock (2007) explain the hostility towards market economies and overall prevalence of leftist ideologies in many highly regulated, often developing countries.

In this paper, we argue that these dynamic political effects of higher and inefficient regulation and corruption can be acerbated by increased political risks that lower economic activity and increase economic distress and social discontent. And if not managed effectively, such dynamics can become entrenched and part of a vicious circle that impedes recovery in a way that Olson has

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described regarding the role of rigidities and vested interests in his seminal book about the rise and fall of nations (Olson 1982).

Section 2 focuses on the ongoing debate regarding Greece's possible exit from the EU, emphasizing political fragmentation, extremism and risk as a source of economic underperformance which in turn revives the so-called Grexit talk. It particularly focuses on Greece and the way that its political market, reacting to the economic crisis provoked by an extremely distorted institutional setting (Mitsopoulos and Pelagidis 2009), has led to an environment that in turn prevents rather than facilitates the recovery of the Greek economy. This follows as a result of the prevailing political risks and extremism, as suggested by the existing literature. These insights suggest also some policy initiatives at the European level and suggestions what developments one can realistically anticipate in Greece from now on. Section 3 concludes.

2. POLITICAL FRAGMENTATION AND RISK AS A SOURCE OF ECONOMIC UNDERPERFORMANCE

As argued in Pelagidis and Mitsopoulos (2014, 2015), European politicians that wanted to support Greece were faced with persistently non-cooperative Greek governments that with their tactics exhausted the goodwill of many and weakened the political positions of those that kept arguing for European solidarity. The Greek economy was of course burdened by the reluctant promotion of much needed reforms that would remove supply side bottlenecks to growth from the Greek economy. While the official creditors pushed for a large "internal devaluation", they allowed the domestic political system to force the cost of this adjustment mainly on the productive sector, where it was less needed as argued in Pelagidis and Mitsopoulos (2014). More crucially, and with the silent acceptance of the official lenders, they largely protected the public sector, where the internal devaluation was much needed. This misguided application of the internal devaluation played havoc with the economy, the labor market, society and in the end political developments, as was easy to foresee (Mitsopoulos and Pelagidis 2009, 2011). Figure 1 shows how employment declined along this process, with political instability and the lack of reform progress placing an cumulative burden on the private sector, where the vast majority of jobs were lost if one excludes the non-renewal of EU-funded job training programs for the young that were not renewed leading to a loss of 80.000 short term jobs in the public sector, early retirement of public sector employees and a few layoffs that were later reversed. This figure also shows how critical the cost of money in the private sector is for the recovery of the economy, a point made also in Mitsopoulos (2015), by depicting the positive correlation between interest rates and the uncertainty the reflect. The significant impact of uncertainty on economic activity is now increasingly documented, as in Bachmann et al (2013), The Economist (2012, 2013) and European Commission (2013).

These developments and findings are compatible with existing work like Pastor and Veronesi (2012, 2013) and Kelly et al. (2014). They analyze the equity risk premium as a function of economic conditions, by decomposing it (Figure 2) into the premium associated with political risks (red) and non-political risks (blue and green). In poor conditions, the odds of a governmental shake-up soar and the political risk premium dominates the equity premium. They point out that political uncertainty commands a risk premium, especially when the economy is weak. The impact is material: by raising the firms' cost of capital, political uncertainty depresses investment and real activity. Furthermore, by raising risk premium, political uncertainty destroys market value. A number of further remarks are also very pertinent to the case of Greece: the political risk is actually larger when the prevailing degree of political uncertainty is high and political institutions are malfunctioning. One should add here also the comment by Klein, in the discussion following Drazen (2001) about the impact of the ability to call elections. It is also larger when economic conditions are weak. In other words, 'political shocks' can have a large adverse impact on stock

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prices and on the real economy, which by any measure should come as no surprise. Finally, a vicious circle between unfortunate economic conditions and high political risk becomes a real gridlock for Greece's economy that cancels recovery and spreads political extremism and business uncertainty. In this context, Kelly, Pastor and Veronesi (2014) emphasize that shortly before key Greek elections one could find a very high price of political uncertainty across all European countries.

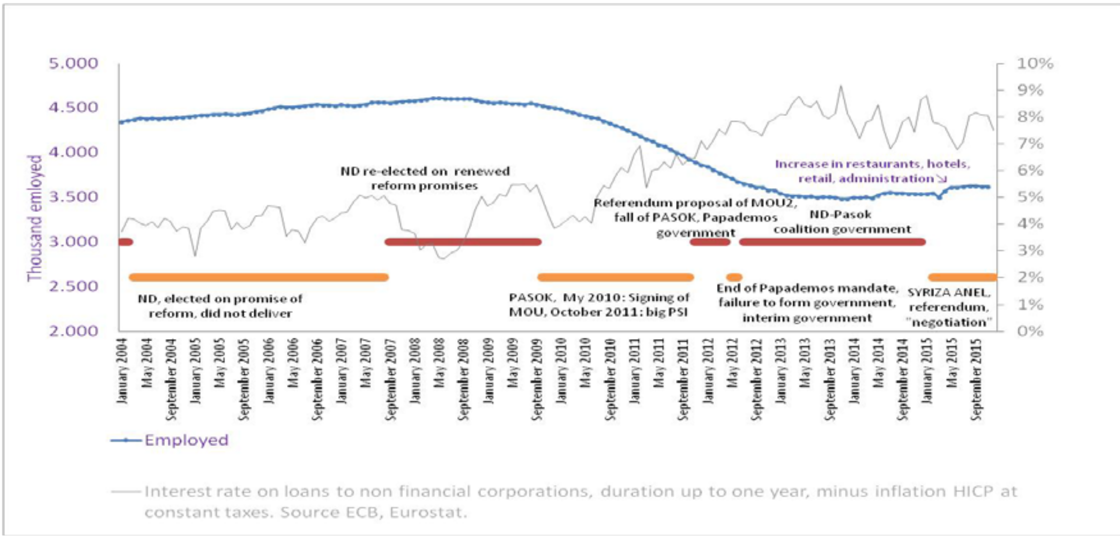


Figure 1. Political risk and economic performance

Source: Authors' elaboration from Elstat data on employment and inflation at constant taxes, Ministry of Interior election results, ECB on interest rates for non-financial corporations.

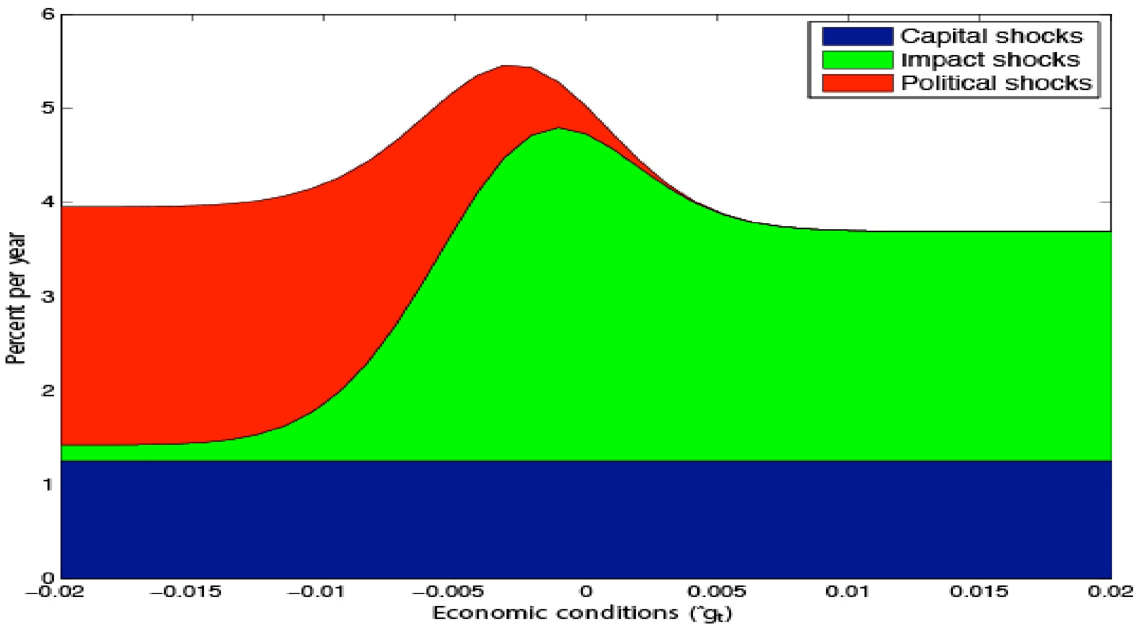


Figure 2. Types of risks
Source: Pastor and Veronesi. (2014)

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As for the political market itself, the typical political reaction to crises is as and Funke, Trebesch, Schularich (2015) argue, that votes for far-right parties increase strongly, government majorities shrink, the fractionalization of parliaments rises and the overall number of parties represented in parliament jumps. These developments likely hinder crisis resolution and contribute to political gridlock. This has in turn important repercussions on growth, incomes, asset prices and employment in the short- and in the long-term, by increasing political uncertainty again by destabilizing and fragment any government and strengthening, in fact, political extremism.

This process is exactly what killed the anemic 0.6% recovery of the Greek economy in 2014, killing the number one priority of increasing demand by boosting business confidence. In fact, in Greece, the party representing the extreme right, the so-called “Golden Dawn”, has gained in repetitive elections since 2012, the fraction of –around- 7-8% of the votes. The currently two largest parties, far left Syriza and center-right New Democracy, in the same period are fluctuating around 55-65% together, meaning that the two-party system is nowadays very weak compared to what it was back in the 90s’ and 00s’ when the two largest parties, socialist PASOK and ND at the time, used to gather together more than 80% of the votes. As a result, the fraction of votes that go to the small parties that appear suddenly and disappear in the election map have increased, together with the increase of the destabilization of the government. It suffices to emphasize that the last ten years the average period the governing period is around two years, as a result of calling early elections, despite that the constitution defines a four year period as the normal period before new elections should be called, which in turn is a result of the design of the constitution (described in Mitsopoulos and Pelagidis 2011, 2016a). Thus, Greece appears (Figure 3) to fit exactly to the model above as ideological fractionalization, number –and votes- of parties in the parliament, weakness of the government and last but not least, opposition voting share have all increased during the crisis, having in turn an unfortunate effect in the recovery of the economy. These developments are in line with the decline in the trust Greeks feel for their government but also EU institutions during the crisis as documented by the annual Eurobarometer surveys.

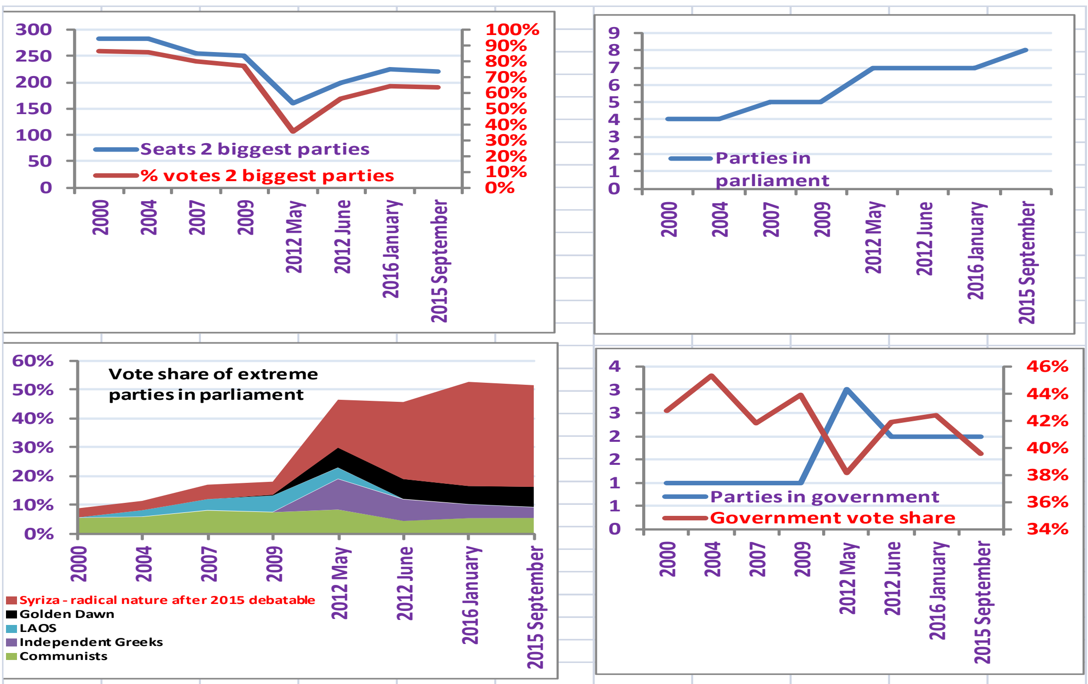


Figure 3. Political reactions extremism in Greece

Source: Greek election results, analysis inspired by Funke, Trebesch, Schularich (2015). LAOS, Independent Greeks are far right and Golden Dawn a Nazi party. The extremism of all votes that support Syriza can be credibly questioned, especially after the 2015 referendum and the signing of the 3rd assistance program MoU.

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These developments document the severe implications the crisis in Greece has had not only on the economy but also on trust in institutions and the capacity of the political establishment to advance meaningful reforms. An ill-fated execution of the initial MoU has weakened the political forces that strived for reform and supported populist extremism that is deeply rooted in the traditions of the clientelistic politics that were in turn the root causes of the crisis. The inability of the incomplete European Union to deal with cases in which domestic politics did not favor the development of national institutions towards the EU standards was resolved with the short-sighted adoption of the “Grexit” threat. This, in turn only increased risks for the productive economy, amplifying the undesirable developments that already were in motion. This fact underscores the need that Europe works out a way to handle such unfortunate events, now and in the future, in a way that both supports “convergence in institutions” among the member states and eliminates the need to resolve to the threat of expulsion, as analyzed in Pelagidis and Mitsopoulos (2015), Mitsopoulos and Pelagidis (2016a, 2016b). Progressing beyond loose coordination of economic policies, even while great progress has been achieved in the area of the Banking Union and fiscal supervision, is key to removing the “Grexit” as a tie-breaking rule in the case Greece or in any other potentially similar future case.

Regarding the developments in Greece, at this stage the damage to the wealth, prosperity and prospects of the country has largely been inflicted. Even if Greeks do not become ever poorer, the path of political radicalization, increased populism and weakened institutions is the baseline scenario history suggests for any country that finds itself in such a situation. The emergence of a reform-oriented political entity that receives broad public support will be the only way out of this situation, and unlikely as it may appear it is not impossible given that a party that offered reforms and fiscal consolidation as a policy platform had actually won close to 50% of the votes in 1990 during quite similar political and economic circumstances, as argued in Pelagidis and Mitsopoulos (2015).

3. CONCLUSION

In this paper we investigate the experience of Quebec and Greece. This comparison focuses on the long term impact that the entrenchment of a secession movement can have on economic activity within the context of a union member that has an economy that is regulated more stringently than the economies of the other union members. The message drawn from this comparison is that the high regulation and overall institutional weakness of Greece forms solid preconditions for a lower long term growth rate, when compared to the average euro are country. This in turn offers a basis for political developments that are conservative with respect to reforms, entrenching a political and economic equilibrium that does not favor an inherent ability to overcome the impasse.

To make matters worse, the amplification of political risks and the pressure excreted on the private economy with the “Grexit talk” have further diminished the ability of domestic politics to promote reforms, shifting the political spectrum towards radicalization and fractionalization amidst an unprecedented economic downturn. These developments are not unusual, and actually they fit well with the predictions made by a growing literature that ties economic regulation with political beliefs and that embeds political risk in socioeconomic developments.

At this stage, the only remaining hope for Greece is that as radical and populist politicians become ever more discredited, a reform-oriented political entity that has the ability to govern and deliver will emerge. At the same time, extreme poverty, loss of wealth and income, overtaxation and lack of expectation for a better future for the majority of the population have to (miraculously) translate into support for such a political entity, as the electorate seeks to regain some sort of normality in their daily lives. Europe could help such developments by taking serious initiatives towards common decision making in basic dimensions of economic policy, giving regulatory and

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institutional convergence among member state more prominence than it did in the past and by allowing a small fiscal space when the projected policies are in the right direction.

References

[1] Agnion P. et al. 2009. *Regulation and Distrust, NBER Political Economy Workshop*. January 7.

[2] Bachmann, R., Elstner, S. and E. Sims, 2013. *Uncertainty and Economic Activity: Evidence from Business Survey Data,* American Economic Journal: Macroeconomics. **5(2):** 217-49.

[3] Drazen, A 2001 *The Political Business Cycle After 25 Years*, in Bernake B. and Rogoff K (eds) NBER Macroeconomics Annual 2001, **Vol 15**.

[4] di Tella, R. & R. McCullock, 2007. *Why Doesn't Capitalism Flow to Poor Countries?", NBER WP 13164*.

[5] Economist, The, 2012. *The Cloud of Uncertainty Dithering in the Dark. Quantifying the Effect of Political Uncertainty on the Global Economy.* (June 16th).

[6] Economist, The, 2013. *Uncertainty and unemployment. (*Jan 23rd).

[7] European Commission 2013. Assessing the Impact of Uncertainty on Consumption and Investment. Volume 12 (2013) Issue 2 - Quarterly Report on the Euro Area. (June 2013). Directorate General for Economic and Financial Affairs (ECOFIN).

[8] Funke M. Schularich M. and Trebesch C., 2015. *Going to Extremes: Politics after Financial Crisis, 1870-2014, CESIFO WORKING PAPER NO. 5553.* CATEGORY 7: MONETARY POLICY AND INTERNATIONAL FINANCE OCTOBER.

[9] Kelly B., Pastor L. and P. Veronesi, 2014. *The price of political uncertainty: Theory and evidence from the option market*. *NBER working paper*.

[10] Mitsopoulos M. and T. Pelagidis, (2009). *Vikings in Greece. The Cato Journal* **29(3):** 399-416.

[11] Mitsopoulos M. & T. Pelagidis, 2016b. How to Forge a Closer and More Democratic Union. Paper submitted to the *Journal of European Integration*.

[12] Mitsopoulos M. & T. Pelagidis, 2016a. *A Model of Constitutional Design and Corruption. European Journal of Law and Economics*. **41(3):** 1-24.

[13] Mitsopoulos M., 2015. Greek export and labor market performance: Facts and myths. XXVII Villa Mondragone International Economic Seminar, Rome, seminar proceedings.

[14] Mitsopoulos M. and T. Pelagidis, 2011. *Understanding the Crisis in Greece*. London: Palgrave/MacMillan. 2012, 2nd revised paperback edition.

[15] Olson M., 1982. *The Rise and Decline of Nations*. Ithaka, Yale University Press.

[16] Pastor L. & Veronesi P., 2012. *Uncertainty about government policy and stock prices*. *Journal of Finance*, **67:** 1219-1264.

[17] Pastor L. & Veronesi, P. 2013. *Political uncertainty and risk premia*. *Journal of Financial Economic.* ***110**: 520-545.*

[18] Pelagidis T. & M. Mitsopoulos, 2014. *Greece: From Exit to Recovery?* Brookings Press.

[19] Pelagidis T. & M. Mitsopoulos, 2015. *Who is to Blame for Greece. Austerity in Charge of fixing a Broken Economy*. London, Palgrave/MacMillan.

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Investigation of impacts of the Transdriatic Pipeline (TAP) Compressor location in the area of Serres Prefecture, application of a methodology to evaluate alternatives

A. Naniopoulos*, G. Kazanas

Department of Civil Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece.
*Corresponding author: Email: naniopou@civil.auth.gr

Abstract

The pinpointing of the GCS01 Compressor Station of the Transadriatic Pipeline (TAP) in the plain of Serres, scheduled by TAP AG, may have a series of negative environmental and social impacts. Among these is air pollution, which is expected to increase due to temperature inversion, driving pollutants into the soil and posing a negative cumulative impact on plantations and humans in the Serres Prefecture. Other impacts include excessive noise levels and extensive impacts on nearby settlements in the event of an accident. For these reasons, four alternative locations for GCS01 are proposed, provided that they do not affect protected or high productivity areas: two by the Serres Prefecture, one by local groups and one by the authors. By performing a Multicriteria Decision Analysis and setting the impacts as criteria, it was found that the best location is the one on Kerdyllion Mountain (marked as ANT1) with the second-ranked appropriate location on Mount Vertiskos (GK1). In conclusion, it is clear that the country can benefit from the construction of the TAP pipeline, but it is important to try to avoid significant negative environmental impacts in this planning phase.

Keywords: pipeline; TransAdriatic Pipeline TAP; natural gas; compressor; environmental impact.

1. INTRODUCTION

The Transadriatic Pipeline (TAP) project was announced in 2003 and will transport natural gas from Azerbaijan via Turkey, Greece, Albania, Adriatic Sea, Italy to the rest of the European countries. In the Greek territory, TAP is 543 km long and is part of the Southern Gas Corridor, through which 10bcm / year of natural gas will be transported in a life cycle of fifty years. The pipeline starts from Kipi Evros, where the first Compressor Station, GCS00, will be settled.

In the future, the capacity of the Transadriatic Pipeline will be increased from 10 to 20 bcm/year. This increase is going to require the development of a new Compressor Station in the Serres Prefecture, the GCS01, with a power of up to 125 MW and operations based on natural gas use [1]. The GCS01 Compressor Station is planned to consist of five compressors (one of which in stand-by mode), with a 25MW power each, and the required area for the development of their premises is 0.17 km^2 [1]. The proposed locations for the construction of GCS01 by the TAP AG, named TAP1, TAP2 and TAP3, are relatively close to each other and are all situated in the plain of Serres, an area with dense agricultural activity and residential uses, including many nearby settlements.

In the Environmental Impacts Study that was developed by the TAP consortium, emissions and other impacts are presented as complying with acceptable limits [1]. However a strong concern has been expressed by local communities, scientific bodies and others, that the actual impacts will be significantly detrimental. It was supported that another, more appropriate location for the

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Compressor Station should be proposed. Thus, this paper first examines the validity of the expressed concerns about possible negative impacts, and secondly it explores and ranks possible alternative locations using a Multicriteria Decision Analysis [2].

1.1 Atmospheric Pollution

The Compressor Station will operate on a 24-hour basis using natural gas, leading to NO_x gas emission. In the area of the Station, NO_x is expected to be recorded from 10 to 20 $\mu g/m^3$ and after construction it is estimated by the TAP company that will reach 50 mg/m^3 before dispersion [1], while the limit for the protection of human health is 40 $\mu g/m^3$ NO_2 and the vegetation protection limit is 30 $\mu g/m^3$ NO_x [3]. Additional emissions are carbon monoxide (CO) while additional emissions include particulate matter (PM2.5) and volatile organic compounds (VOCs) [4] that are currently not considered by the TAP study.

The phenomenon of temperature inversion seems to be intensive in the selected area, since it is a plain's basin surrounded by mountains. During the day, as a result of the earth heating by the sun, instability is caused in the lower part of the atmosphere, which is in contact with the ground. As a result, pollutants are trapped between the earth surface and the tallest stable layer of the atmosphere [5]. This phenomenon deteriorates air pollution and leads to soil acidification as gaseous pollutants are deposited on the soil [6].

Such a type of air pollution has been proven to have negative impacts on human health. More specifically, nitrogen oxides, combined with volatile organic compounds and sunlight, create smog and tropospheric ozone [7]. Inhalation of such smog can cause shortness of breath, wheezing and respiratory problems. It has also been cited as a potential cause of problems, such as asthma and lung malfunction [8]. Concerning the particulate matter PM2.5, its particles have an aerodynamic diameter of equal or less than 2.5 μm and are considered to be the most hazardous, since due to their small size, they are able to reach deeper into the lungs, and may result in respiratory and cardiovascular problems [9]. 90% of the particles are respirable and PM2.5 inhalation causes various forms of pneumoconiosis, asthma, and even in some cases cancer [6].

These negative impacts affect not only humans, but also other species, such as bees. It has been proved that Nitrogen dioxide and oxides of nitrogen (NOx) affect and impair the ability of bees to detect the scent of flowers and therefore their very source of nutrition. This could cause serious negative consequences for the volume of bee colonies and subsequently for the pollination of agricultural crops [10].

Another crucial point is that the MM5 weather model which was used for the Environmental Impacts Study (presented by the TAP consortium) is suitable for locations with an average altitude of 1.500 m., while the location in the Serres plain, where the GCS01 Compressor Station will be constructed, has a 15 m. altitude above sea level and the actual height of the Compressor Station emissions would be at a range between 350 and 400 m. above sea level. Moreover, the HYSPLIT pollutant dispersion model, which was used in the Environmental Impacts Study, forecasts average pollutant concentrations for long periods, but not peak concentrations in short periods of time. It has been reported that one should look at peak exposures, as compared to the averages over longer periods of time, since it seems that they are more biologically relevant if the health effect is triggered by a high, short-term dose rather than a steady dose throughout the day [11]. Last but not least, the data provided by the National Weather Service Station in Serres, which has been in continuous operation for over 50 years, were not connected with or used by the Environmental Impacts Study [12].

1.2 Noise emissions

The emitted noise, according to the TAP study, will amount to 65 db (A). This level corresponds to industrial areas, according to Greek Legislation. The selected area is rural, not industrial, with no background noise, and thus the perceived noise annoyance will be much higher. Hence the

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maximum permissible limit should be even less than 50 db (A), which is the limit in urban areas [13].

1.3 Accident risk

The risk for accidents is also significant, since in the event of an accident-explosion in a Compressor Station, the radius of the shock wave can reach up 3.5 to 4 km away [12,14], within an area containing many residential settlements. Indicative is the fact that 47% of accidents on gas pipelines are related to compressor stations and facilities, according to the Transportation Safety Board of Canada [15]. Based on recent experience, the zone that may be affected in such an accident is quite extensive [16]; in the 1989 explosion near the Russian city Ufa, the radius of destruction reached 4 km, according to a New York Times report [17]. The affected zone in the plain of Serres, in the case of an accident analogous to the Ufa explosion, is shown in Figure 1. The total population number that will be possibly affected is up to 6720 residents, dispersed in the settlements of Skoutari (2154), Neos Skopos (1934), Neochori (1227), Monovrisi (566), Agia Eleni (476), Konstantinato (332) and Krinos (31), population according to the 2011 Greek census [18].

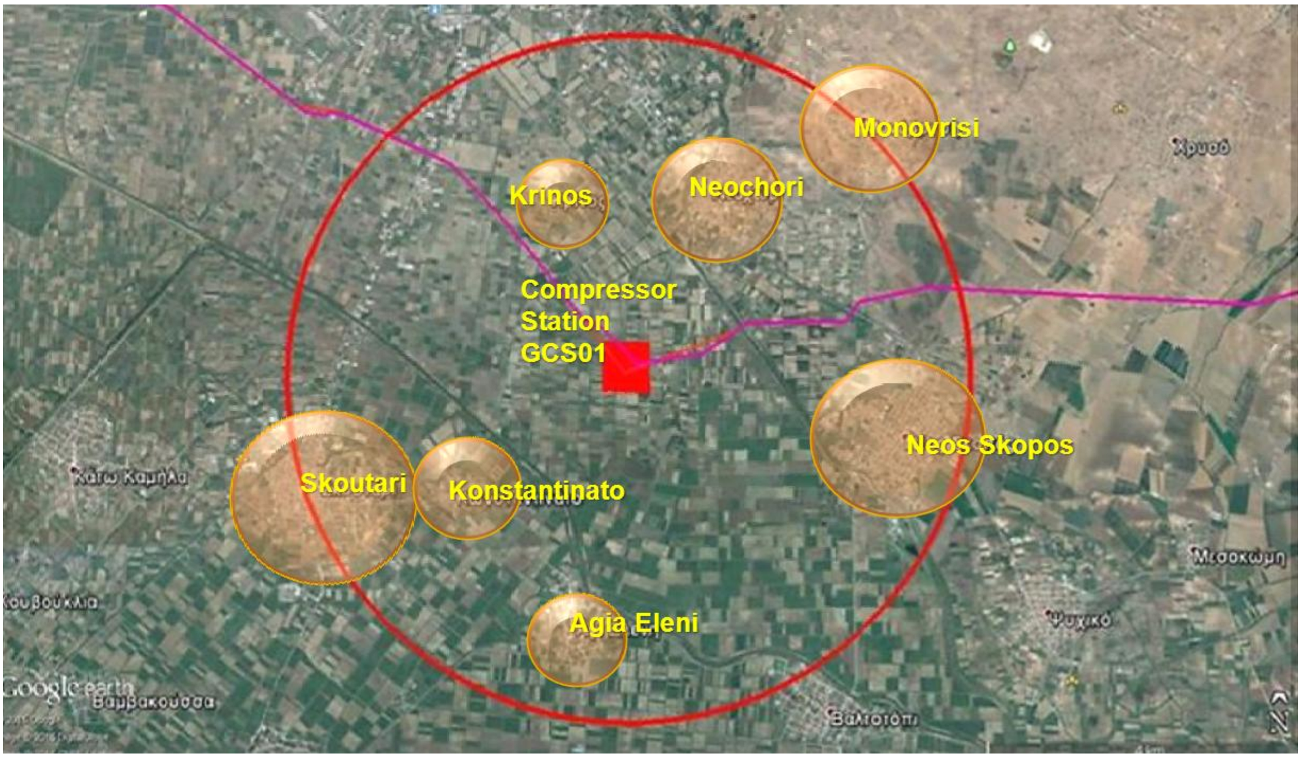


Figure 1. Radius of destruction in the plain of Serres, in the event of an accident analogous to the Ufa explosion.

The risk could be considered as even higher than the above, as the plain of Serres is a seismogenic area and specifically on a Composite Seismogenic Source (CSS) [19]. In conjunction with seismicity and modern strain data, CSSs can be used for regional probabilistic seismic hazard assessment and for investigating larger-scale geodynamic processes, according to the Greek Database of Seismogenic Sources [19].

1.3 Concluding remarks concerning the proposed TAP locations

Concerning the three, proposed by TAP, alternative locations for the GCS01 Compressor Station, it was concluded that they are connected with a series of possible negative consequences on the area

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of the Serres plain, hosting dense residential and agricultural activity. Among these are air pollution - expected to increase due to temperature inversion - that will cause deposition of the pollutants on the soil, posing a cumulative negative impact on plants and humans in Serres Prefecture, and the high expected noise level causing annoyance to the surrounding settlements. Moreover, the area is seismogenic and the impacts on nearby settlements, in the event of an accident will be extended. Thus there is a need for alternative locations to be proposed, evaluated and selected.

2. METHODOLOGY FOR SELECTING AND EVALUATING ALTERNATIVE LOCATIONS FOR THE GCS01 COMPRESSOR STATION

2.1 Selection of alternative locations for the Compressor Station GCS01

Two alternative locations for the Compressor Station GCS01 were proposed by the Serres Prefecture (locations OTA1 and OTA2), one by local groups (location ANT1) and one by the authors (location GK1). OTA1 is located 20 km west of the city of Serres and OTA2 25.5 km east. ANT1 is located 5.02 km northwest of Asprovalta on Kerdyllion Mountain, and GK1 10.22 km west of Nigrita on Mount Vertiskos. The alternative locations were carefully selected to be outside NATURA 2000 protected areas, as shown in Figure 2, where with red colour are marked Special Protection Areas (for bird protection) and with blue colour are marked Special Areas of Conservation and Sites of Community Importance [20]. In addition, these locations are away from residential settlements, in contrast to the TAP proposed locations. The evaluation of these alternative locations was a complex problem with several parameters. Hence, the Multicriteria Decision Analysis Method (MCDA) was selected as an appropriate methodology for their evaluation and ranking.

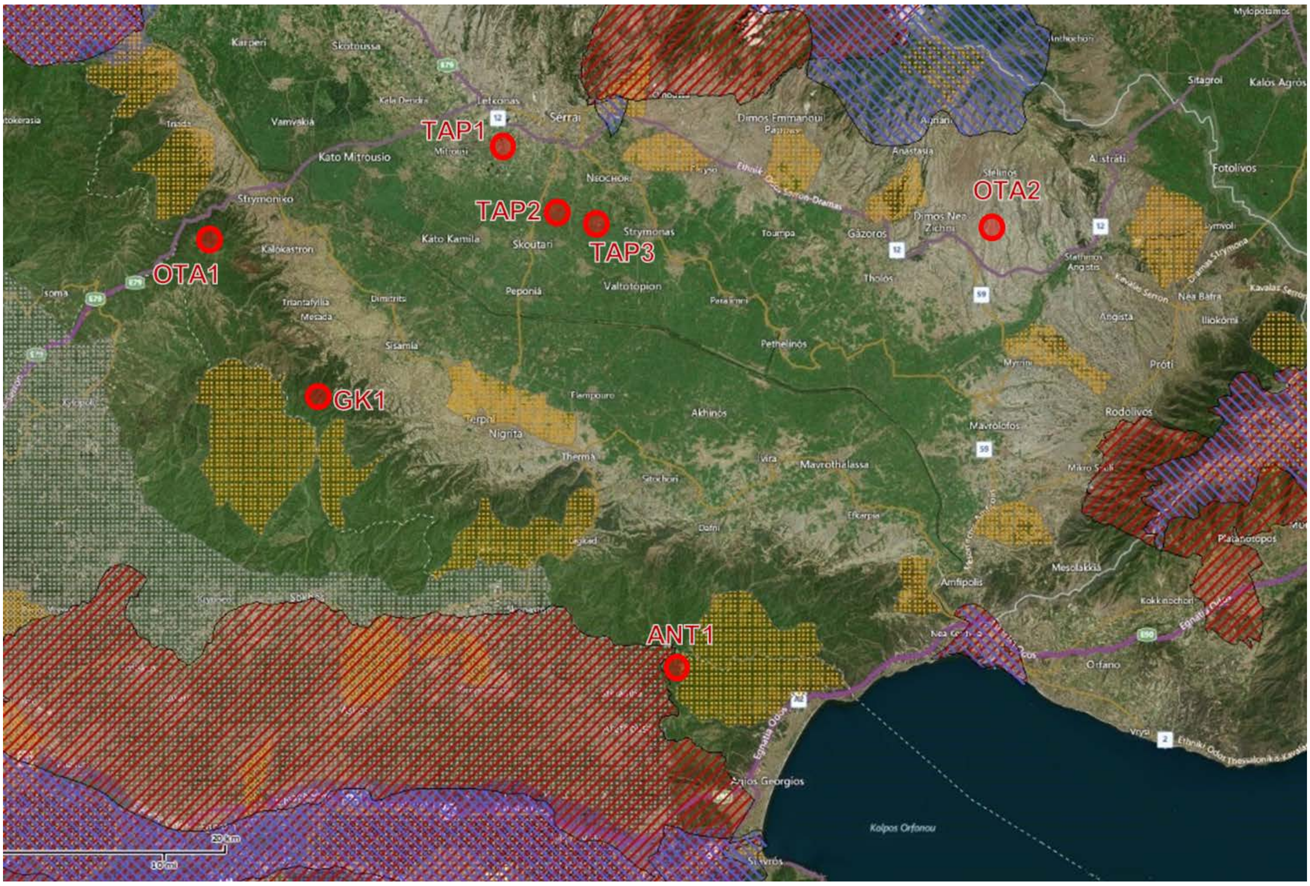


Figure 2. The three TAP proposed locations and the four alternative locations for the Compressor Station GCS01.

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2.2 Evaluation of alternative locations for the Compressor Station GCS01

The Multicriteria Decision Analysis Method was performed by setting carefully selected criteria and alternatives. The factors ‘project development cost’, ‘aquifer pollution’, ‘soil pollution’, ‘air pollution’, ‘noise and vibrations’, ‘accident risk’, ‘socio-psychological factors’ and ‘effect on local activities’ were selected as criteria K_j. Each table row in Table 1 corresponds to one of the seven alternative GCS01 Compressor Station locations E_i. Subsequently, weights B_j for each criterion and rankings per criterion and alternative were set in a scale of zero to ten (0-10). The total rank AE_i for each alternative location is given by the Equation 1. The proposed locations by the TAP consortium, i.e. TAP1, TAP2 and TAP3, are physically close to each other, within a distance of less than 4 km, thus only one of them was evaluated since they have similar characteristics and it seems that TAP3 is the preferred one by TAP consortium.

$$AE_i=\Sigma(B_j*E_iK_j)\ ,\ \ i=[1\ldots7]\ ,\ j=[1\ldots8] \qquad (1)$$

In Equation 1, E_iK_j is the ranking per criterion and alternative in a scale of zero to ten (0-10). Among the sums AE_i, the minimum one is selected as the best, as the weights are set higher for more negative impact. On this basis all the alternative locations were evaluated as shown in Table 1.

The weights of the different criteria were set by the authors taking into consideration, for each one, its nature and special characteristics according to the location. Other stakeholders may provide their own assessments since what is followed here is a transparent process. Hereafter the weights setting by the authors is explained and discussed.

Table 1. Multicriteria Decision Analysis Method for alternative locations of Compressor Station GCS01 evaluation.

Criterion		**K_1**	**K_2**	**K_3**	**K_4**	**K_5**	**K_6**	**K_7**	**K_8**	
Alternative		**Project development cost**	**Aquifer pollution**	**Soil pollution**	**Air pollution**	**Noise and vibrations**	**Accident risk**	**Socio-psychological factors**	**Impact on local activities**	**AE_i**
E_1	TAP1	3	7	7	5	6	9	7	8	376
E_2	TAP2	3	7	7	5	6	9	7	8	376
E_3	TAP3	3	7	7	5	6	9	7	8	376
E_4	OTA1	7	3	3	2	4	7	6	6	239
E_5	OTA2	4	4	4	3	4	7	6	7	266
E_6	ANT1	8	2	2	1	2	3	5	4	146
E_7	GK1	7	3	3	2	3	3	5	5	183
	Weight	1	8	9	7	8	9	6	6	
		B_1	**B_2**	**B_3**	**B_4**	**B_5**	**B_6**	**B_7**	**B_8**	

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The first criterion was the 'Project development cost', which includes costs for land acquisition and construction. The weight of this criterion was estimated as the lowest one, taking into consideration the tremendous economic benefits, of the TAP consortium, from the TAP operation and also the permanent character of negative effects to the local communities and the Prefecture of Serres in general.

Weights for the three pollution criteria (Aquifer pollution, Soil pollution, Air pollution) were set high in a range from 9 to 7 and consequently the E_iK_j ranking was also high, in a range from 7 to 5, for the TAP selected areas in the plain of Serres, where the phenomenon of temperature inversion occurs causing the accumulation of pollutants with high negative effects on humans and also agricultural and animal production. Additionally, locations close to residential or other settlements were ranked with a high E_iK_j, in a range from 9 to 7, as far as it concerns the criteria of accident risk and impact on local activities. Locations ANT1 and GK1 are characterised by a high altitude, 560 m. and 524 m. respectively [21] and a distance from residential and other settlements. Hence, the E_iK_j rank ranges between 1 and 3, concerning the criteria of noise and pollution.

Objections against the three TAP proposed locations, include also the fact that aquifer is close to land surface, with a local minimum depth of 1 m, according to data provided by the Prefecture of Serres. In addition, the land value in the area of Skoutari and Neos Skopos is among the highest within the Serres Prefecture. These facts lead to low E_iK_j ranking in project development cost, equal to 3 points (the lower in this criterion) and the higher E_iK_j ranking in aquifer pollution, equal to 7 points.

The noise by the Compressor Station, as explained earlier, is going to be continuous and unceasing, and therefore acquires considerable weight as a criterion, set equal to 8. The location ANT1 is characterised by high altitude and safe distance from residential areas, which is more than 5 km away. However, there should be provision for sound effects in the natural environment (forest animals, insects etc.), that is why rating was set to 2. For GK1 location, which is more than 4.7 km away from the closest village, the rating was increased by one. The locations OTA1 and OTA2 are equally away from the nearest residential settlement, so their rank was set the same for both.

The criterion K7 includes the social and psychological factors and the reactions of local communities, related to the acceptance of the selected Compressor Station location by the locals. Therefore, the rank for each alternative is clearly dependant on the distance from settlements, facilities and agricultural areas.

The eighth criterion is the impact on local activities. These activities include premises and buildings, where people work, study or play sports. These facilities are: the Hippotherapy Centre located in Neos Skopos one of the two existing in Greece, the Serres Technological School, the Omonoia Athletic Park, the Greek Sugar Industry and the neighbouring industrial area, where every day hundreds of people work and move. In this criterion areas, such as workplaces or places where people accumulate, are considered. Hence, the locations on the Serres plain were ranked with the highest rating for this criterion (8 points). OTA2 was ranked with 7, OTA1 with 6, GK1 with 5 and ANT1 with 4 points as it is the most remote from settlements location. It should be mentioned that the criterion weight for the last two criteria was set equal to 6 as their significance is quite important, but lower than that of the criteria K2-K6, because there is the possibility of financing certain activities and premises to relocate in safer locations.

3. RESULTS AND DISCUSSION

The performing of a Multicriteria Decision Analysis yielded ANT1 location, on Kerdyllion Mountain, as the best solution, with an AE_i sum equal to 146 points and as second-ranked, in terms of appropriateness, GK1 location, on Mount Vertiskos, with an AE_i sum equal to 183 points. It is possible to construct the GCS01 Station at the GK1 location with a small deviation, of 11 km, compared to the already designed pipeline route by TAP AG.

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The two above locations, having emerged as the optimal alternative solutions, do not seem to affect nearby settlements, in terms of accident risk and noise, as their distance from them is equal or more than 5 km. These locations are also characterised by a high altitude, potentially allowing for a better dispersion of air pollutants. They are also outside Natura 2000 protected areas. The TAP proposed locations are expressed by very high negative AE_i sum, thus they should be reconsidered.

Assuming that appropriate provisions are taken, air pollution could be probably reduced by using appropriate filters and increasing the height of chimneys significantly. Noise could be reduced by means of appropriate insulations. It seems that what could not be reduced is the probability of an accident, which is exacerbated by the fact that the area is seismogenic. Thus a change of the TAP selected location of GCS01 Station seems to be necessary.

Considering the whole consultation process with local communities, as performed by the TAP consortium, it seems that those affected should be given appropriate documentation and scientific support in clarifying their questions and concerns. The Environmental Impact Assessment Study is a very lengthy document, not easily comprehensible by non-scientists, thus probably a certain budget should be foreseen, in the cases of such high-impact projects, for local communities to conduct their own independent evaluation of the plans and the assessment of potential impacts.

4. CONCLUSIONS

In conclusion, it is clear that the country can benefit from the construction of the TAP pipeline, but it is important, in this planning phase, to try to avoid significant negative environmental impacts by selecting an alternative location for the GCS01 Compressor Station. This location should be in compliance both with the needs of the construction project and the requirements of the physical and built environment. In this paper, the performed Multicriteria Decision Analysis designated ANT1 location on Kerdyllion Mountain as the optimal solution, and GK1 location on Mount Vertiskos as the second best one, among these considered in the present study. The proposed by the TAP consortium locations were disqualified because of their proximity to a large number of villages and settlements, accident risks and other negative environmental impacts, which are assessed rather inadequately in the present TAP Environmental Impact Assessment Study.

References

[1] E.ON New Build and Technology GmbH, 2013. *Environmental and Social Impact Assessment (ESIA).* Trans Adriatic Pipeline AG, Athens.

[2] http://www.openness-project.eu/library/reference-book/sp-MCDA (accessed September 23rd, 2015).

[3] Council of Ministers Act 34/2002 (Official Governmental Gazette 125/A/5-6-2002).

[4] http://www.environmentalhealthproject.org/files/Summary%20Compressor-station-emissions-and-health-impacts-02.24.2015.pdf (accessed September 14th, 2015).

[5] Papagiannis & Roussos, 2012. Valuation of external costs by the emission of particulate matter in the lignite mining. Metsovion National Technical University, Athens.

[6] Fytianos & Samara–Konstantinou, 2009. *Environmental chemistry*. University Studio Press, Thessaloniki.

[7] Soufla, 2013. *Study of air pollutants in the city of Patra with the method of analysis in principal components*. University of Patra, Patra.

[8] Filippidou & Koukouliata, 2011. *The impact of climate change on the respiratory system*. First Respiratory Clinic–Technical and Sanitary Inspection Department of Kavala Hospital, Kavala.

[9] Lianou, 2010. *Study of personal exposure to airborne particles of physicochemical characteristics and sources in indoor residential areas: investigation of the contribution of the external environment and municipal activities in indoor aerosols*. Technical University of Crete -Faculty of Environmental Engineering, Chania.

[10] Girling, R.D., Lusebrink, I.D., Farthing, E., Newman, T.A. & Poppy, M.G., 2013. Diesel exhaust rapidly degrades floral odours used by honeybees. *Scientific Reports 3*, Article number 2779.

[11] Darrow L.A., Klein M., Sarnat J.A., Mulholland, Strickland M.J., Sarnat S.E., Russell A., Tolbert P.E., 2011. The use of alternative pollutant metrics in time-series studies of ambient air pollution and respiratory emergency department visits. *Journal of Exposure Science and Environmental Epidemiology*, **21(1)**, 10–19.

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C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
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[12] http://antitap.blogspot.gr/ (accessed September 7th, 2015).
[13] Presidential Decree 1180/81 (Official Governmental Gazette 293/A/6-10-1981).
[14] Geotechnical Chamber of Greece–Department Eastern Macedonia, 2013. *General opinions of our Department on the Environmental and Social Impact Assessment and the TAP pipeline route.* Geotechnical Chamber of Greece–Department Eastern Macedonia, Kavala.
[15] http://www.tsb.gc.ca/eng/ (accessed October 5th, 2015).
[16] Novozhilov V., 2001. Review of investigations on rising fireballs and new implications for mitigation of hazardous fuel releases. *Proceeding of 5th Asia-Oceania Symposium on Fire Science and Technology* (eds. M. A. Delichatsios, B. Z. Dlugogorski and E. M. Kennedy), December 3–6, Newcastle, Australia, Vol 1, 144-155.
[17] http://www.nytimes.com/1989/06/05/world/500-on-2-trains-reported-killed-by-soviet-gas-pipeline-explosion.html (accessed October 2nd, 2015).
[18] http://www.statistics.gr/el/2011-census-pop-hous (accessed October 4th, 2015).
[19] Sboras S., Caputo R., Pavlides S., Chatzipetros A., Papathanasiou G. and Valkaniotis S., 2009. The Greek Database of seismogenic sources (GREDASS): State-of-the-art. *Proceedings of the 28th National Congress GNGTS*, November 16–19, Trieste, Italy, Vol 1.1, 126–128.
[20] http://natura2000.eea.europa.eu/ (accessed September 21st, 2015).
[21] http://www.helppost.gr/xartes/ypsometro-evresi/ (accessed October 1st, 2015).

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Towards a strategic research agenda on soil, land-use and land management in Europe

T. Panagopoulos*, V. Ferreira, M. D. Antunes

Research Center for Spatial and Organizational Dynamics (CIEO), University of Algarve, Gambelas Campus, 8000 Faro, Portugal
*Corresponding author: Email: tpanago@ualg.pt

Abstract

Towards a strategic research agenda (SRA) on soil, land-use and land management in Europe, it was collected relevant national information on research demands for Portugal, based on key stakeholder interviews, a workshop and desk exercise. Priority societal challenges that were emphasised during this investigation were the food security and safety, the secure supplies of safe drinking water, and the reduction of raw material and resource consumption. According to National Key Stakeholders (NKSs) the specific topics (research needs) that should be included in the European SRA, were prioritised as follows: planning soil conservation; opportunities of innovative and sustainable agricultural technologies; strategies for soil/water pollution minimization and remediation; combating desertification; promoting urban green infrastructure; sustainable urban planning and brownfield redevelopment; impact of agricultural policies; competition between land uses; soil system mapping and monitoring; and resource efficient economy. It was highlighted the need to improve the dissemination procedure and was suggested enlarged stakeholder's involvement in the future research projects to increase application of research in practice and face effectively the local needs. Furthermore, stakeholders consider important to facilitate the access to databases and scientific publications through thematic online platforms, and improving the management and identification of national research projects. The dissemination of projects should include indicators to access the social impacts, policy implications and demonstrations of applicability, in addition to publications and public presentations. Notwithstanding some funding schemes were indicated as opportunities for future research, the NKSs recommend strategic partnerships between universities and enterprises, and a clear and accessible cost-benefits analysis, to increase the added value of research. The societal challenges facing Europe increasingly require research and innovation which integrates different approaches from across research disciplines. These often increase the impact and usefulness of the research for businesses and society. Concluding the inquiry, the NKSs consolidated recommendations on the future projects, which should promote interdisciplinary teams, integrate economic, social and environmental aspects, ensure mixed funding establishments, and guaranty social acceptance and findings applicability.

Keywords: strategic research agenda; soil; land-use; land management

1. INTRODUCTION

There are many synergistic or competing potentials uses of limited land resource, which can impact the linked soil-sediment-water system (SSW). Protecting land and SSW system is critical to balance the demand and supply of ecosystem goods and our natural capital, to cope with the effects of several driving forces and to decrease the global footprint of human made production and consumption activities. To design sustainable strategies of land management and to decide from alternative uses of land it is indispensable to determine the biophysical and socio-economic

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indicators and causes of resource degradation, both through scientific knowledge and from the perception of local populations [1, 2]. Research is necessary in order to steward land to a more sustainable future for Europe's citizens and its global partners.

Policy, on the other hand, is essential because governments can promote the wise use and management of land. The instruments include local, regional and international laws, agreements or programs, and public education is probably the most important tool in the long run. Unfortunately, one of the reasons for inadequate implementation and adoption of sustainable land management is the lack of adequate mechanisms and channels for scientific knowledge transmission, and dialogue between science and police-makers [3, 4]. There is an urgent need to improve communication of scientific findings such that they inform policy at all levels. For that, the completed knowledge on land degradation must be interdisciplinary and have cross-sector approaches, providing a deeper insight into the socio-economic and policy aspects [5]. To ensure such interdisciplinary, the research methods must extend over the academic boundaries, enabling non-academic stakeholder engagement and the inclusion of practical questions.

Multi-stakeholder approach is increasingly being promoted and implemented in social, environmental, and sustainability management research. Many studies have advocated and demonstrated the importance of the stakeholder participation (as land-users, decision makers or experts) as an integral component over the development of some sustainable management initiatives and strategies [6,7,8 and 9]. The iterative process, that includes knowledge exchange between scientists and potential users, it is fundamental not only to facilitate the application of valuable scientific knowledge on practice, but also to inform scientists about research needs and priorities from decision and policy-makers perspectives [8, 10]. Such information would be beneficial to consolidate research agendas and programmes, addressing challenging and multi-faceted problems [9, 11]. The involvement of key stakeholders helps to take into account local realities, strengths, and constraints when developing appropriate strategies, and can also reduce the level of conflict among participants [6]. Stakeholders based research creates a sense of ownership over the process and outcomes, and could increase the likelihood that knowledge and evidence will be used on practice decisions and policies, thus increasing their quality and durability [7, 8].

In that context arises the project INSPIRATION (Integrated Spatial PlannIng, land-use and soil management Research Action), financed from European Union under the Horizon 2020 program. The consortium comprises 21 partners from 16 European countries. The project aims to establish and promote the adoption of a strategic research agenda (SRA) for land-use, land-use changes and the related, impacted SSW system in order to meet current and future societal challenges and needs facing Europe. For that, a specific methodology was applied, in each country, to collected information on research and innovation needs, experiences and suggestions regarding connecting science to policy/practice, and existing and promising national and transnational funding schemes. This paper presents relevant national information for Portugal.

2. MATERIALS AND METHODS

The multi-national methodology was based on a multi-stakeholder and interdisciplinary approach, applied by National Focal Points (NFPs) working as knowledge exchange facilitators. Before the procedures to collect information, as for the other countries, in Portugal, a group of National Key Stakeholders (NKSs) was defined in order to include a variety of stakeholders from public bodies, business, scientific community, society, and relevant funders, across the various soil and land management disciplines [12].

Different approaches have been used to review research themes, identify knowledge gaps, questions and indicators from stakeholders, and develop research agendas for environmental management [9, 11]. On this project, it was applied personal questionnaires by interview, performed

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a desk study and organized a final 2-day workshop discussion [13]. The outcomes of the collation of demands for research are taken up and reviewed following a conceptual model described in the next section.

2.1. Conceptual Model

The main EU-societal-challenges which are expressed in the Horizon 2020 work programmes inherently straddle disciplinary boundaries and changes in one sector can have undesirable and unexpected consequences in another. These challenges must be tackled to benefit from the land and the SSW system and still to protect the natural capital and resources. Consequently, such challenges should be met on the SRA development process, and research topics must demand for multi-dimensional and intra-disciplinary approaches. Therefore, in order to identify cross-country and cross-sectoral knowledge gaps, research questions are structured along four overarching perspectives within a conceptual model (Figure 1).

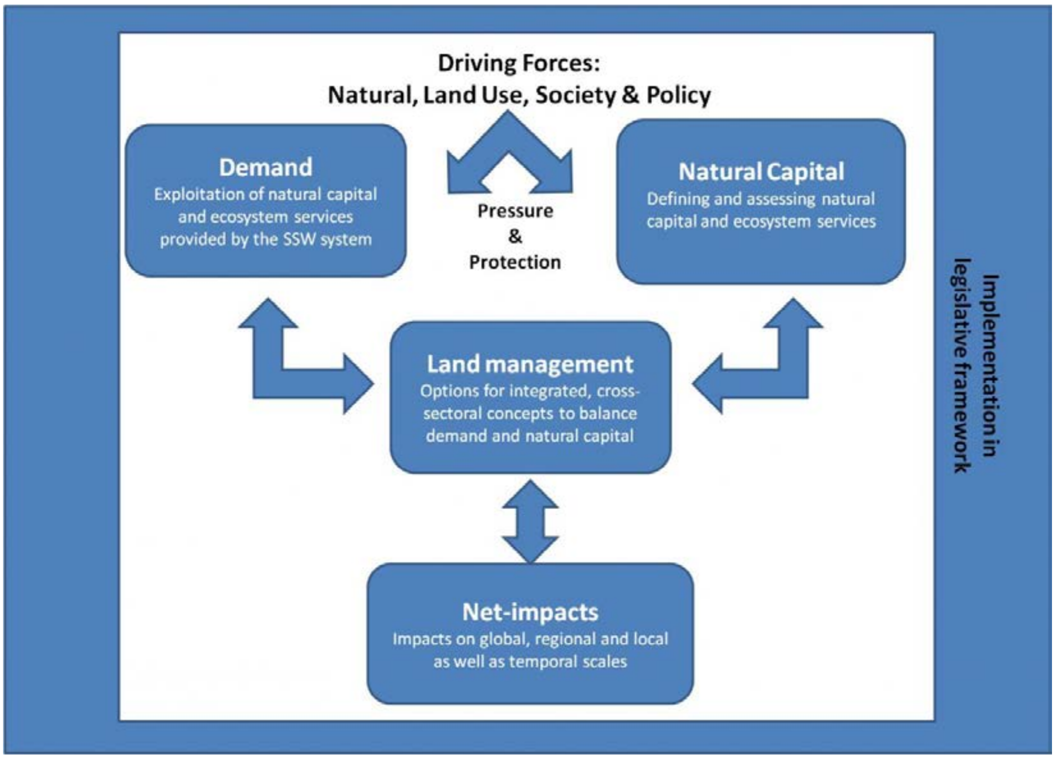


Figure 1- Conceptual framework of the project Inspiration [14].

This conceptual model assumes the importance of land and the SSW systems as goods and natural capital stocks. However, there are multiple natural, land-use, society and policy drivers which affect these natural resources, their potentials and as well as their use, contributing to ecosystem degradation. An imminent question is the conflicting interests regarding land-use among the relevant stakeholders in a society (farmers, land planners, citizens, etc.), that leads to the paradigm of 'Either-Or': expectations of land-users towards maximizing economic benefits of natural resources stocks and goods on the one hand, and maximum requirements from societal groups towards different protective regulations on the other. Therefore, the sustainable management of land resources (agricultural, forest and urban) has to follow integrated, cross-sectoral concepts concerning the different demands of stakeholders. And lastly, on this process of natural capital management, the economic, societal, administrative and political impacts have to be assessed. Thus the net-impacts on a local, regional and global as well as temporal scale are significant back-coupling effects and determinants of crucial importance [14].

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The proposed conceptual model arises from the recognition of such complexity, necessary to take into account when analyzing the national situations and formulating the SRA around. It links four themes: resource demand and efficiency; defining and assessing natural capital; land management; and net-impacts on global, regional and local scale. Summarily, these themes aim to group research gaps concerning sustainable land management stewardship along four questions [14]:

- Demand: What does society demand from natural capital and ecosystem services including the SSW-system?
- Natural capital: What has nature, including the SSW-system to offer and which determinants sustain the system?
- Land management: What are options for an integrated, cross-sectoral land management to balance societal demands and natural capital?
- Net impacts: What are the impacts of different options of managing natural capital, including the SSW-system on global, regional and local as well as temporal scales?

2.2. Desk exercise

The desk-exercise was done since the beginning, complementary to the methods mentioned, and the obtained information can be seen as supportive/underpinning to the information provided by the NKSs. Via a desk-exercise NFPs investigated, organised, and summarized information obtained through interviews and workshop (publications, reports, etc.). This step was particularly important to identify/verify relevant documents, programmes or agendas suggested by interviewees. Moreover, it was essential to structure research questions according the conceptual model.

2.3. NKSs interviews

The personal questionnaires and interviews are common methods and aim to point stakeholders own perspectives. A questionnaire template for interviews of the NKSs by the NFPs was prepared [15]. The template is meant as a guide with sample questions and points of attention for the discussion with the NKSs. It is not prescriptive and not restrictive, the topics in the questionnaire are guiding and sample questions can be used as example. The questionnaire aims to obtain the information needed to give a foundation to the SRA at national levels regarding three mainly domains: research & innovation needs; connecting science - policy/practice; national and international funding organisations and schemes. In Portugal, 20 NKSs were interviewed and selected to represent different disciplines and institutional backgrounds including: land-use planners; managers; soil, sediment and water experts; researchers, funders and regulators/policy makers.

2.4. Two-day NKSs workshop

Workshops were mentioned has beneficial as "learning space", in which the sharing of experiences can foster learning for participants and lead to new, creative ways of thinking about the process-based challenges [16]. It was organized at national level a 2-day workshop (Figure 2) where the collated information (NKSs interviews and desk-exercise) was reviewed, synthesized and prioritized by the NFPs, under NFPs facilitation.

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Figure 2 – Two-day workshop sessions in Faro, Portugal.

The workshop in Portugal took place at the University of the Algarve on 6-7 November, 2015. More than 20 experts from public and private funding institutions, research organizations, industry, NGO and regulation participated in the workshop, including the interview applicants. The workshop focused on different sections (Figure 2).

After receiving the NKSs, NFPs made an informative presentation about the INSPIRATION project, and review and synthetize information already collected by interview and desk-exercise. Afterwards, NFPs facilitated three parallel sessions for discussion according the key domains (strategic research agenda topics, science-policy interface and possibilities for funding). Finally, conclusions were drawn up in a plenary session where the results of the three parallel theme groups were presented and integrated.

3. RESULTS AND DISCUSSION

3.1. Societal challenges

Societal challenges were discussed during the interviews, since it is inevitably connected to the topics to be included in the SRA, and may be used as bases for defining of the overarching themes for aggregating such research needs. On the graphic it's shown the percentage of NKSs answers for each challenge (Figure 3).

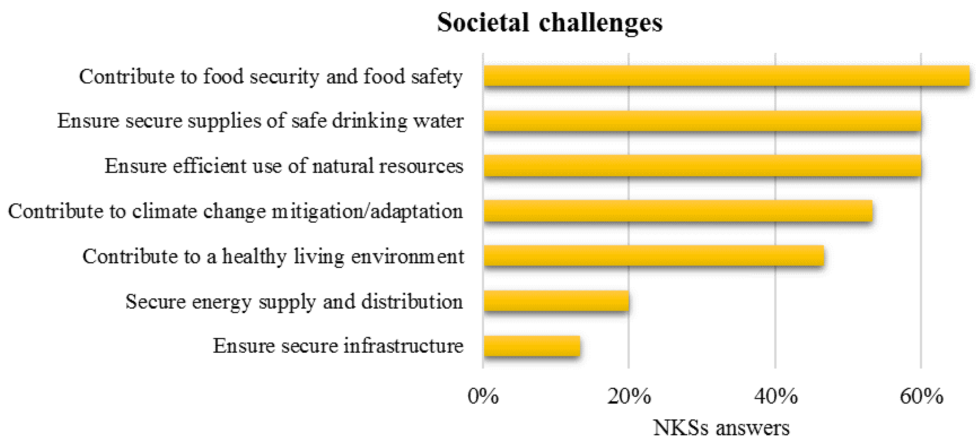


Figure 3 – Percentage of NKSs answers to which societal challenges they consider more important.

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Contribute to food security and food safety, ensure secure supplies of safe drinking water, and ensure efficient use of natural resources are societal challenges more frequently mentioned as priority and urgent for Europe, during the interviews and the workshop. Contribute to climate change mitigation/adaptation and contribute to healthy living environment are also important challenges with more than 50% of NKSs answers. Secure energy supply and distribution and secure infrastructure were considered less priority comparatively to the other challenges.

3.2. Research needs/topics for the SRA

A synthesis of specific topics to include the SRA, indicated by the NKSs in Portugal, was done. It was reported many research questions aggregated in main ten topics. Below the research topics were summarized according to the interview and workshop discussions about why it is relevant and form whom, who will be affected and responsible. The specific questions were arranged according the conceptual model through desk exercise.

PT1. Soil Conservation - Sustainable land management, soil fertility, soil regeneration, carbon soil sequestration, social awareness.
PT2. Opportunities of innovative and sustainable agricultural technologies - Organic farming; sustainable practices; potential productivity of land; waste compost options; water use efficiency.
PT3. Strategies for minimization and remediation of soil/water pollution
PT4. Combating desertification - climate change, soil erosion and land degradation
PT5. Promoting urban green infrastructure - grass management; urban agriculture; green-roofs.
PT6. Urban planning and redevelopment - Brownfields redevelopment; multicultural cities; Ageing; Shrinking cities.
PT7. Impact of agricultural policies - Environmental effects; socio-economic transformations; rural development.
PT8. Competition between land-uses - land-use efficiency; bioenergy demand
PT9. Soil system mapping and monitoring
PT10. Resource Efficient Economy with a Sustainable Supply of Raw Materials -Multifunctional forest; Mediterranean landscape; non-wood forest products

3.3. Science-policy-practice

"Scientific knowledge" was essentially described, by NKSs in Portugal, as the acquired new knowledge obtained through scientific methods, including practice, experimentation and validation, to achieve specific objectives. NKSs revealed to use newly knowledge regularly and fundamentally to support land management, planning and decision making process, to produce innovative new products and methods, and also, on the academic field for dissemination through writing papers and teaching. The mainly sources to learn about are the scientific papers, conferences, reports and data bases (Figure 4). Television and newspapers are the lowest mentioned.

Depending on their position and sector, NKSs were involved on the formulation of research questions, or on doing scientific research, or synthetizing it for policies and decisions. Some suggestions were done so that the obtained knowledge, from future scientific research, can be useful in practice and known in the wider society, namely: improve the results dissemination; include the involvement with the stakeholders/entities in the future research projects; facilitate the access to data bases and scientific publications through online platforms; improve the management and identification of national research projects through a platform; monitoring the practical application of policies and actions; valorize human resources; and improve connections between regional entities. Institutional barriers, conflicts of interest, gap between research and society, unclear investigation objectives, bureaucracies and the thematic concentration should be avoided.

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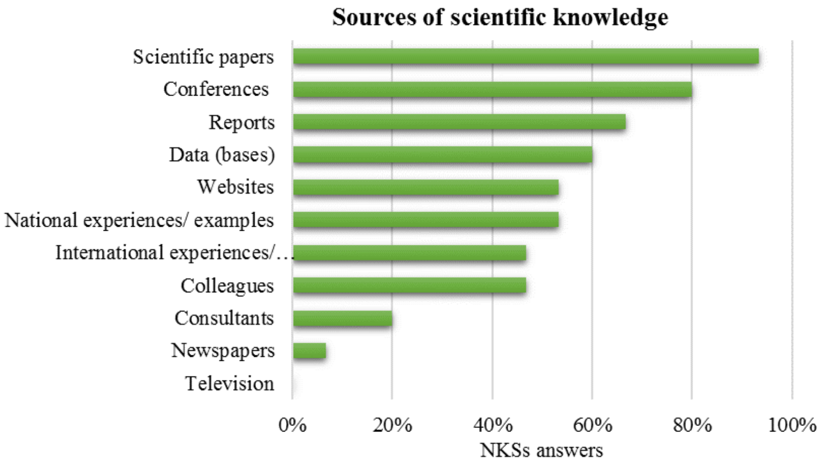


Figure 4 - Percentage weight of answers from NKSs in Portugal to question: Which sources of (scientific) knowledge do you use for doing your job?

3.4. Funding schemes

Several regional, national, European and international funding schemes were suggested by NKSs that could offer opportunities for research on soil, land-use and land management. Some NKSs consider the current funding options successful because usually promotes the creation of networks for continuation of research, but other reflects the low applicability of the research results on decisions or policies. To overcome it, they consider indispensable the requirement of the practice component in the funding programs, with the results demonstration and divulgation. On the other hand, the establishment of demonstrators set visibility to the results of the research, and the marketing of the results it's considered fundamental to get fund and recognized by the research funding communities. NKSs reflect during workshop sessions that it would be essential that scientific results from ongoing and finished projects are available through dissemination platforms (including cost outcomes assessment), for information, coordination and for awareness of possible future partnerships. It also could help to avoid the funding on already studied aspects.

To increase the added-value of different financial resources for doing research that contributes to national and EU demands, NKSs consider fundamental a higher connection between research institutions and enterprises with specific and possible connected needs for scientific knowledge. There is general consensus that public-private partnerships can be a solution. It was also discussed the potential of multidisciplinary research projects and programs to achieve a multiplier of monetary funds. Though, NKSs think that to avoid the difficulty to recognize some integrated approaches related to land-use and management and SSW systems, it's necessary the definition of target sectors for research funding, that represent a line and mechanism with not only social and economic objectives but also concerning ecosystem sustainability.

The projects findings should be emphasized near local and regional communities so that people can understand that research funding money is necessary for the country development and sustainability. On the last 40 years there was an evolution on the environment policies, however it's necessary to develop the population culture and awareness in environmental questions.

4. CONCLUSIONS

The societal challenges facing Europe increasingly require research and innovation which integrates different approaches from across research disciplines. These often increase the impact and utility of the research for businesses and other users. Towards the elaboration of European SRA on land and SSW management, specific information was collected and analysed for Portugal. A clear vision of

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research state-of-the-art, needs/priorities, difficulties between science and practice/policy and funding prospects were obtained strategically among stakeholders.

Concluding the national activities of INSPIRATION project, it can be perceived that Portuguese NKSs are conscious about land degradation pressures and its effects, and on the need of innovative and sustainable ways of land management. Besides, aware of some difficulties and gaps on science-practice interface and funding processes, NKSs consolidated recommendations on the future research projects on soil, land-use and management, which should promote interdisciplinary teams, integrate economic, social and environmental aspects regarding priorities and topics mentioned, ensure linkage between research institutes and companies facilitating funding establishments, and guaranty social acceptance and findings applicability.

References

[1] Lindskog, P. and Tengberg, A., 1994. Land degradation, natural resources and local knowledge in the Sahel zone of Burkina Faso. *GeoJournal*, **33 (4)**, 365-375.

[2] Sal, A.G. and García, A.G. 2007. A comprehensive assessment of multifunctional agricultural land-use systems in Spain using a multi-dimensional evaluative model. *Agriculture, Ecosystems & Environment*, **120 (1),** 82-91.

[3] Grainger, A. 2009. The role of science in implementing international environmental agreements: The case of desertification. L*and Degradation and Development*, **20 (4)**, 410–430.

[4] Thomas, R.J, Akhtar-Schuster, M., Stringer, L.C., Marques, M.J., Escadafal, R., Abraham, E., Enne, G. 2012. Fertile ground? Options for a science-policy platform for land. *Environmental Science & Policy*, **16**, 122–135.

[5] Escadafal, R., Marques, M. J., Stringer, L. C., and Akhtar-Schuster, M. 2015. Opening the Door to Policy relevant, Interdisciplinary Research on Land Degradation and Development. L*and Degradation and Development*, **26**, 409–412. doi: 10.1002/ldr.2403.

[6] Inam, A., Adamowski, J., Halbe, J., and Prasher, S. 2015. Using causal loop diagrams for the initialization of stakeholder engagement in soil salinity management in agricultural watersheds in developing countries: A case study in the Rechna Doab watershed, Pakistan. *Journal of Environmental Management*, **152**, 251-267.

[7] Reed, M.S., 2008. Stakeholder participation for environmental management: a literature review. *Biological Conservation*, **141**, 2417-2431

[8] Cvitanic, C., Hobday, A.J, van Kerkhoff, L., Wilson, S.K. and Dobbs, K. 2015. Improving knowledge exchange among scientists and decision-makers to facilitate the adaptive governance of marine resources: A review of knowledge and research needs. *Ocean & Coastal Management*, **112**, 25-35

[9] Fazey, I., Bunse, L., Msika, J., Pinke, M., Preedy, K., Evely, A.C., Lambert, E., Hastings, E., Morris, S., Reed, M.S., 2014. Evaluating knowledge exchange in interdisciplinary and multi-stakeholder research. *Global Environmental Change*, **25**, 204-220.

[10] Dilling, L. and Lemos, M.C. 2011. Creating usable science: Opportunities and constraints for climate knowledge use and their implications for science policy. *Global Environmental Change*, **21 (2)**, 680-689.

[11] Fazey, I., Evely, A.C., Reed, M.R., Stringer, L.C., Kruijsen, J.H.J., White, P.C.L., Newsham, A., Jin, L., Cortazzi, M., Phillipson, J., Blackstock, K.L., Entwistle, N., Sheate, W.R., Armstrong, F., Blackmore, C., Fazey, J.A., Ingram, J., Gregson, J., Lowe, P., Morton, S., Trevitt, C., 2013. Knowledge exchange: a review and research agenda for environmental management. *Environmental Conservation*, **40**, 19–36

[12] Maring, L., Ferber, U., Dictor, M.C., Starzewska-Sikorska, A., Klusáček, P., Panagopoulos, T., Bal, N., Tabasso, M., Cotič, B., Nathanail, P., Garcia, G., Pütz, M., Finka, M., Zechmeister-Boltenstern, S., Dumitru, M., Rehunen, A., Brils, J., 2015. Memorandum of Understanding on how the National Focal Points should execute their tasks. Final version as of 30.04.2015 of deliverable D2.2 of the HORIZON 2020 project INSPIRATION. EC Grant agreement no: 642372, UBA: Dessau-Roßlau, Germany.

[13] Bartke, S., Grimski, D., Brils, J., Makeschin, F., Nathanail, P., Darmendrail, D., 2015. ½ year activity reports. Public summary as of 01.11.2015 of deliverable D1.1 of the HORIZON 2020 project INSPIRATION. EC Grant agreement no: 642372, UBA: Dessau-Roßlau, Germany.

[14] INSPIRATION, 2016. Integrated Spatial PlannIng, land use and soil management Research Action. (www.inspiration-h2020.eu, accessed February, 2016).

[15] Brils, J., Maring, L., Darmendrail, D., Dictor, M.C., Guerin, V., Coussy, S., Finka, M., Bal, N., Menger, P., Rehunnen, A., Zeyer, J., Schröter-Schlaack, C., Villeneuve, J., Gorgon, J., Bartke, S., 2015. Template for national information collation. Update 1 version as of 02.07.2015 of deliverable D2.3 of the HORIZON 2020 project INSPIRATION. EC Grant agreement no: 642372, UBA: Dessau-Roßlau, Germany.

[16] Stringer, L.C., Twyman, C., Gibbs, L.M., 2008. Learning from the South: Common challenges and solutions for small-scale farming. *The Geographical Journal*, **174**, 235–250.

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The connection between the GDP and the WTE investments in global scale

K. Patsiouras[1,2*], C. S. Psomopoulos[2,4], I. Venetis[3], A. Bourtsalas[4], N. J. Themelis[4]

[1] Department of Mechanical Engineer, University of Applied Sciences,
250 Thivon & P. Rali Ave, GR-12244, Egaleo, Greece.
[2] Department of Electrical Engineer, University of Applied Sciences,
250 Thivon & P.Rali Ave, GR-12244, Egaleo, Greece.
[3] Department of Economics, University of Patras, GR26504, Rio, Greece.
[4] Earth Engineering Center, Columbia University, U.S.A. Columbia University,
500 West 120th St., New York, NY 10027, U.S.A.
*Corresponding author: Email: kpatsiouras@hotmail.com

Abstract

Waste to Energy (WTE), is a compound method of waste management and energy production. Over the last 10 years, countries that have developed economically, have invested in the Waste to Energy solution and thus creating thousands of jobs. In addition, a new market was established, for the simple reason that countries like Sweden, not just invested in this solution for maximum utilization of the waste, but created a new service for other countries that do not afford that waste treatment method. Furthermore, Waste to Energy technology is considered as a Renewable Energy Source and the main reason is that MSW (Municipal Solid Wastes) are endless and as the years passing by, waste generation is going to increase dramatically. As a result of what is stated above, WTE investments give a huge upward boost to the GDP of countries which, first of all, spend millions in the landfill and CO_2 emissions fines and to import fossil fuels (oil, natural gas) for their energy needs.

Keywords: Waste to Energy technology; GDP; waste management; MSW; waste;

1. INTRODUCTION

Wastes management is a common problem for every country on planet Earth, from the smallest one to biggest. The policy and the waste management methods are different in every country though. The main reason for that matter is the GDP of each country which controls the financial part of the waste management which of course is the most crucial [1, 2]. According to the Environmental Protection Agency, there are some steps in order to minimize the impact caused from the municipality solid wastes (WTE). First of all is the prevention and the minimization is coming after. Re-use and recycling are the next steps in an optimal way of waste management. Finally, energy recovery is the last waste management method before the waste disposal in a landfill [1, 2, 3, 4].

The Waste to Energy method is as mentioned above, a waste management method and at the same time an energy production source. Today, there are over 1.000 WtE facilities operating around the globe which treat hundreds of millions of waste and produce huge amounts of electricity and heat. The basic drawback of this waste management method is the initial financial cost which is very big compared with recycling plants or landfills [1, 5, 6, 7]. Of course as years passing by, the amount of wastes produced by people is going to increase. The Waste to Energy method, by many aspects is the most beneficial way of waste management and countries with high GDP/capita, invest on this method in order to gain from the multi-beneficial results.

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2. WASTE MANAGEMENT METHODS AND INVESTMENTS IN EUROPE

At the beginning of the financial crisis (2010) in Europe, each person generated about 468kg of municipality wastes in a yearly scale. Four years later (2014), with the economic crisis affecting Europe greatly, the municipality waste generation has been increased to 481kg per person. The main reason for this phenomenon is the population increase of European Union as well as the GDP/capita increase of some major economies such as Germany. [3, 4, 5]

2.1 Waste Management and GDP/capita in Europe in 2010.

In 2010, 22% from the total amount of waste generated from the European citizens, was treated with the Waste to Energy method while, 40% was recycled and 38% was going to the landfills. As it was stated above, WTE method is an expensive and high cost method so it was developed by countries with high GDP/capita and good financial state. For example, Germany, after the 2005 landfill ban, developed the WTE method and as a result, 35% of their wastes were treated with the WTE procedure while 65% was recycled. Another great example is Sweden. In Sweden, 49% of the MSW was treated in WTE plants while the other 51% was recycled. On the other hand, there are countries in the European Union which are not so financially developed and they were considering other matters as priorities and not the waste management. As a result, for example in Cyprus 20% of the municipal wastes was recycled and the rest 80% was going to landfills. Another example is Bulgaria in which 100% of the wastes generated, were going to landfills. Figure 1 presents the Waste Management in Europe in 2010 and Figure 2 presents the GDP/capita situation of these countries in 2010 [3, 5, 8, 9].

Based on the figures 1 and 2, it is obvious that countries with high GDP/capita invest large amounts of money in the Waste to Energy technology in order to achieve the optimal waste management solution. Countries with low GDP/capita, choose the landfills as the final destination of the majority of their wastes because they cannot afford the waste to energy technology.

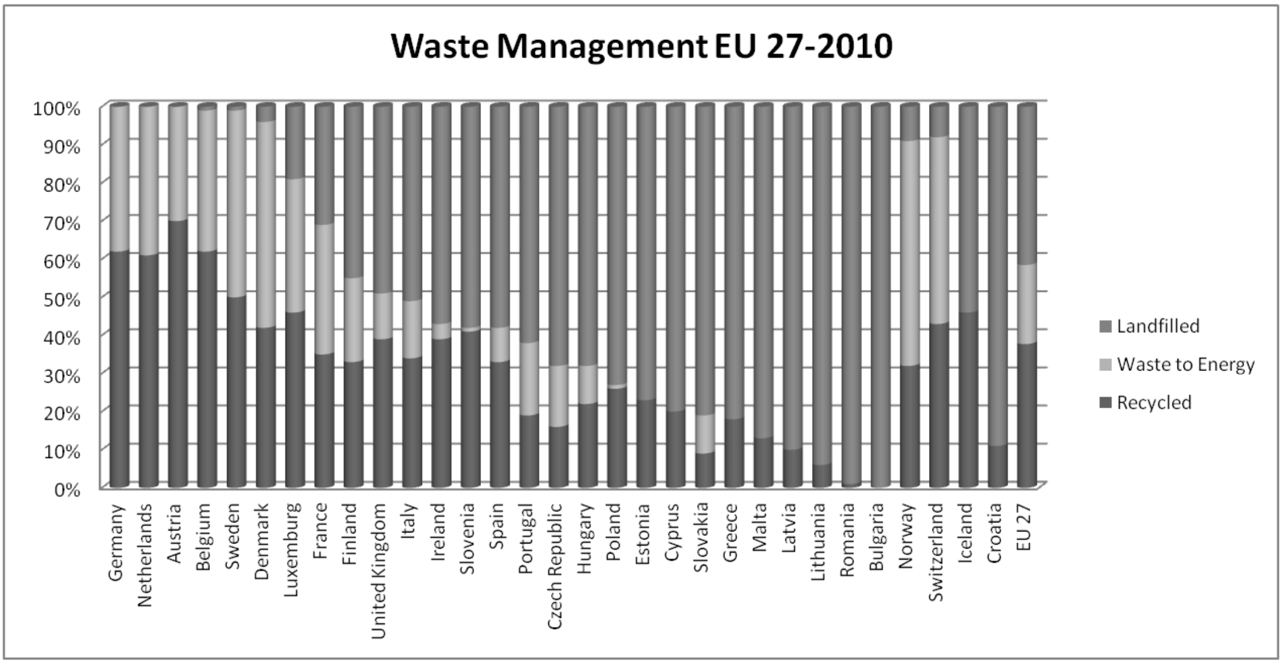


Figure 1: Waste management methods and percentages in Europe, 2010.

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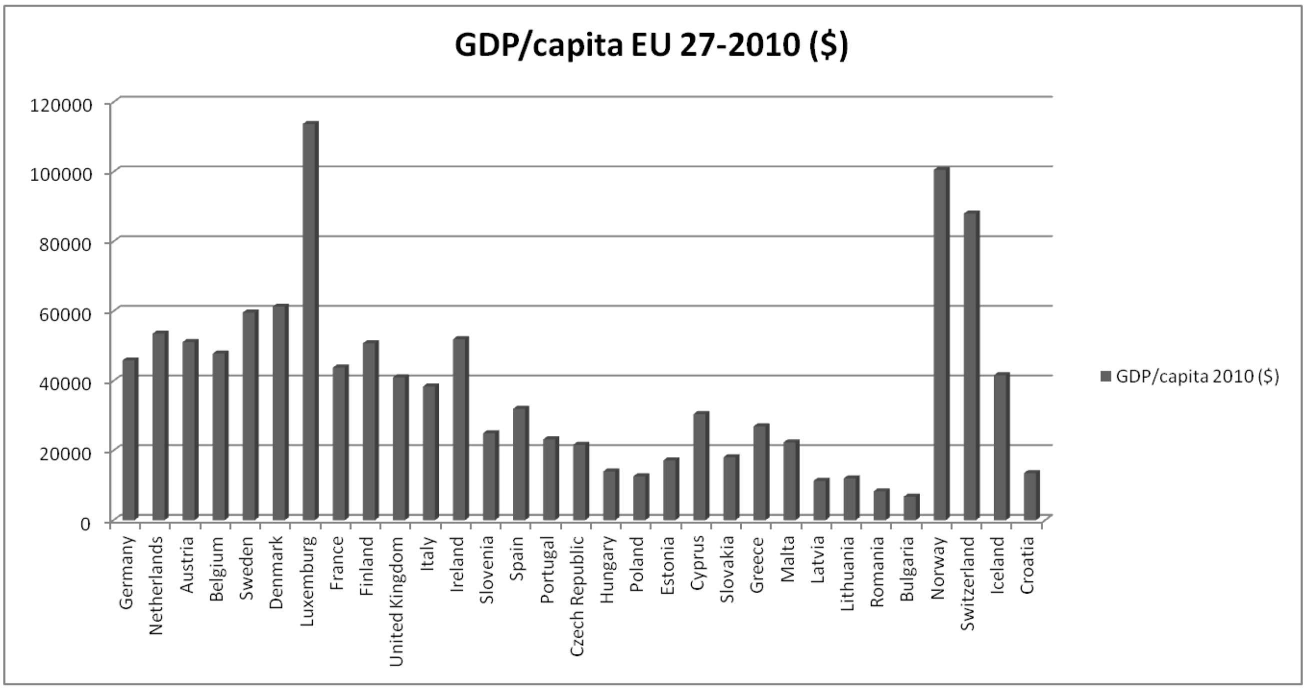


Figure 2: GDP/capita of the European countries in 2010.

2.2 Waste Management and GDP/capita in Europe in 2014.

In 2014, many changes have been made since 2010 in the Waste to Energy Technology investments. Specifically, countries which had an increase in their GDP/capita, invested more money in the Waste to Energy technology. Although the financial crisis presence was still staying strong, countries like Estonia, Bulgaria and Lithuania which had a very low GDP/capita, decided to invest in the Waste to Energy Technology. Furthermore, countries like Switzerland, Norway and Denmark maintained their big investments in the Waste to Energy, transforming a waste management method to a very profitable financial method. Figure 3 presents the Waste Management situation in 2014-2015 in EU and Figure 4 presents the GDP/capita of these countries at the end of 2014.

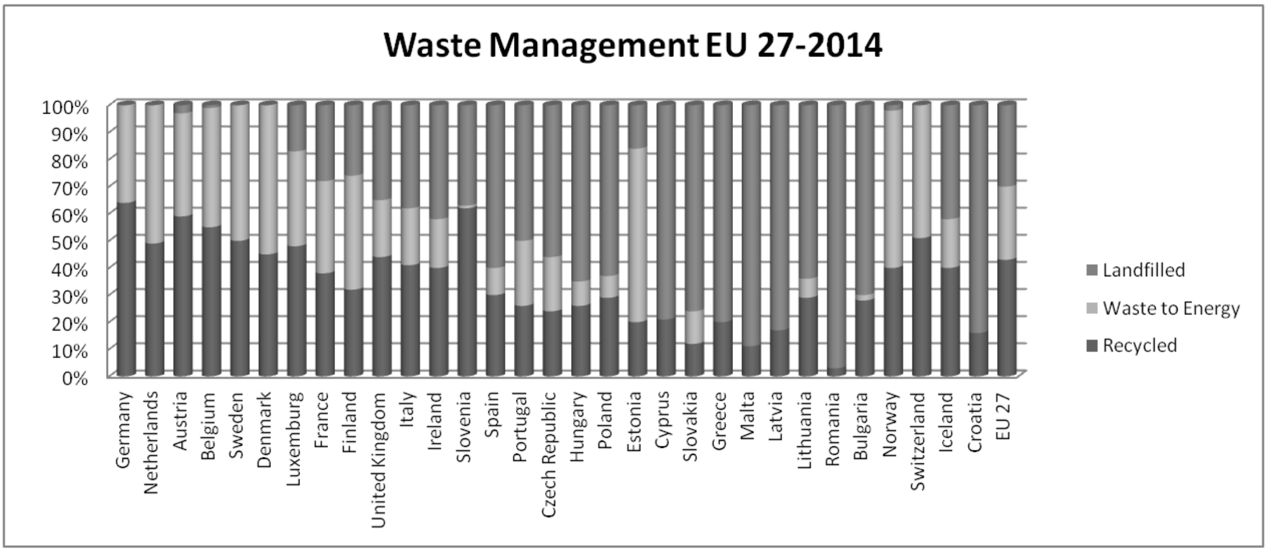


Figure 3: Waste management methods and percentages in Europe, 2014.

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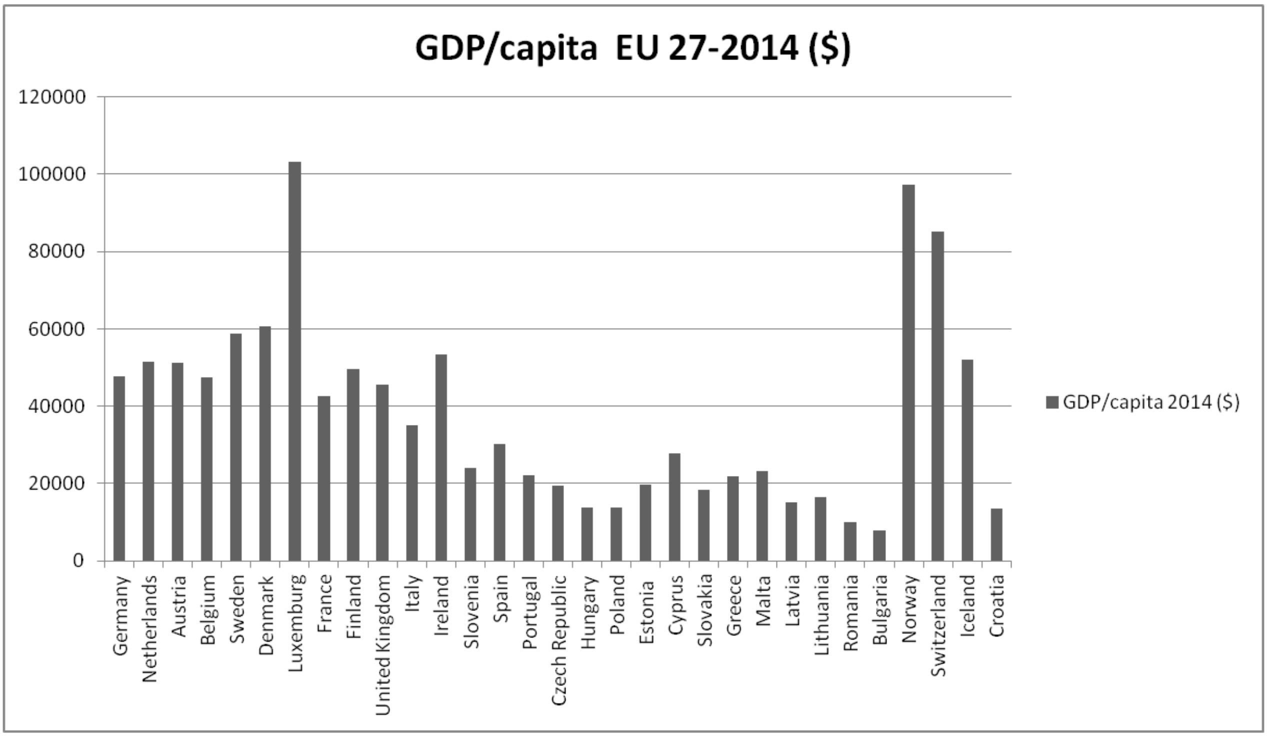


Figure 4: GDP/capita of the European countries in 2014.

First of all, it is obvious that every country which had an increase in their GDP/capita, it also showed an increase of the WTE technology usage. Countries like Germany, Sweden, Netherlands, Denmark, Belgium and many others, treat at least 35% of their wastes via the WTE procedure. Also, countries like Switzerland and Norway invested big in this method and as a result the WTE plants in these countries, treat more than 50% of their MSW. Finally it is obvious, that there is a tendency by European countries for new investments in the WTE technology which could be observed from the increase in the WTE usage in waste treatment from 20% in 2010, to 29% in 2014[5, 8, 9].

2.3 Waste Management and GDP/capita in the Rest of the World

United States of America have shown a huge interest in the WTE technology from the late 80's and combined with an increase of 10% of the GDP/capita(2010-2014), they used large amounts of money in the optimization of this technology. As a result, in United States of America, the 7.6% of the total MSW generated is processed at waste-to-energy facilities while 63.5% is going to landfills. The outcome of the WTE technology usage in USA is that 30 million tons of trash per year is treated, producing about 2.800 MWh of electricity. Also, many facilities sell steam for heating directly to end users such as industries, office buildings and civilian houses [5, 6, 7, 10].

Africa and Latin America are 2 parts of this planet in which WTE technology is something unknown and the major reason is the extremely low GDP/capita and the bad financial situation these areas are into. There are investment plans and ideas on the table, because in these regions, billions of wastes produced each year and except a small amount of them which will be recycled, the rest of them are going to landfills and dumpsites. Unfortunately, the countries there are not so stable in many aspects so the risk of an investment of an ''outsider'' will be big [3, 5, 11].

Australia is considered as a goldmine for the WTE companies. First of all, 18 million tons of waste produced each year in Australia. There are over 30 sanitary landfills which produce huge amounts of CO2 and other gasses result a huge impact in the environment. Although Australia has a high GDP/capita, the country policy and investments are not involved with waste management. A contract of a 400 million WTE plant has been signed in January 2016, its construction will be

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completed at the end of 2018 and it will receive wastes from six different council areas, producing electricity for 35.000 households [12, 13].

Asia is consists of 54 states, 6 of them are dependent territories. From the 48 Asian states, except from Japan, Korea, China and India, the rest of the countries have a very low GDP/capita and as a result their waste generation is going to dumpsites and illegal landfills without control and inspection. From the other 6 countries, only Taiwan which is a province of the People's Republic of China, has developed and invested the WTE technology [8].

As it was mentioned above, GDP/capita is a key factor in the WTE investments. Nevertheless, there are countries like **Japan** which although they suffered a significant decrease in the GDP/capita from the 2010 to 2014 of about -23%, the policy of the Government led to new investments in the WTE technology. As a result, from a total of 55 million tons of wastes produced each year in Japan, about 38 million tons are treated in Waste to Energy plants which were increased from 250 in 2010, to 370 in 2014. Japan is considered as the largest user of WTE technology worldwide [5, 14, 10, 15]. On the other hand, **China**, which is considered as one of the world's fastest developed countries, from the late 90's started to invest big in the WTE technology. China is the verification of the rule of the dependence of the WTE investments and the GDP/capita of a country. China in 2010 had already 77 WTE plants in its territory operating, treating about 23 million tons of wastes (15% of the total MSW generated. In 2014, 4 years later and with an increase of about 32% in its GDP/capita, 13 more WTE plants started their operation, treating about 30 million tons per year (20% of the total MSW generated). Finally, the Government of China has announced the construction of another 200 WTE plants until 2020, following the path of Sweden in the Waste Management policy and one of these plants in the town of Shenzhen will be the largest WTE facility in the world with yearly waste treatment of about 1.825.000 tons of wastes [5, 10, 16, 17]. **Taiwan,** is a great example of a country which invested big in the Waste to Energy technology. Taiwan, like China is one of the fastest developed countries worldwide. Taiwan's GDP/capita was approximately 30.525 $ in 2006 and only 10 years later it is increased significantly (40%) to 43.599 $. Another admirable thing about this country is the fact that although its GDP/capita went high, the MSW generation reduced from 8.900.000 tons of waste per year in 2000, to 8.000.000 tons of waste per year in 2010. That is a considerable achievement considering the fact that GDP/capita and Waste Generation are two co-depending values. Nevertheless, Taiwan has 26 operating WTE facilities which are treating about 50% of the MSW produced and 2 more plants will be operating until 2020 [5, 18, 19]. **India,** is a country with a huge GDP/capita growth over 100% (from 729$ to 1518$ in the last 10 years. India is the second goldmine for WTE companies and the obvious reason is that 227.000.000 tons of wastes are generated each year. Unfortunately for the waste management sector, the policy of the financial growth of the country is based on the development in energy sector and the waste management is far behind. The fact that only 51% of the wastes generated are collected says it all. At 2008, 2 WTE plants and one RDF plant (Refuse-derived-fuel) are operating in India treating about 1.1 million tons of wastes each year, a tiny amount compared to the total MSW generation. Indian Government stated in an Environmental Conference in 2015 that until 2025, over 50 million tons of wastes will be treated with the thermal procedure in WTE plants [3, 5, 8]. Finally, **Korea** is a country with a relevant financial growth and a good GDP/capita value. The environmental and waste management policy is the same as China and Japan. At 1995, the total amount of MSW produced in Korea was about 18 million tons of wastes, from which 23% was recycled and composted, 6% was thermally treated and the rest 71% went to landfills. In only 15 years, these percentages became completely different which means that huge investments were made and changed the waste management sector completely. Specifically, the amount of wastes produced from Korean citizens in 2010 was about 19 million tons of wastes from which 58% was recycled and composted, 23% was thermally treated in WTE facilities and only 19% was going to landfills. In 2016, there are over 60 WTE facilities which treat about 6 million tons of wastes each year [20, 21].

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CONCLUSIONS

This work examined the importance of the GDP/capita and the connection that it has, concerning the Waste-to-Energy Development and Investments. A huge increase in the amount of investments has been observed specifically over the last 15 years in the WTE sector. The reason that this method is so more beneficial than other waste management methods is that it is not only a simple waste management method but it is also an environmental friendly way for energy production. As it was also mentioned above, it is an expensive waste management- energy production method and that is why, developed and highly developing countries invest to it.

As the years passing by, landfills and dumpsites should be banned for the optimal preservation of the environment. As the latest trends showed, many WTE plants will be developed and operate in the following years in many countries so first of all, all these billions of tons of wastes which end up in landfills will be treated properly and produce millions of MWh of electricity and heat and save huge amounts of CO2 which would be produced from fossil fuels usage.

REFERENCES

[1] Mavropoulos, A., 2010. Waste Management 2030+, Waste Management World.

[2] http://www.cewep.eu/ (accessed April 10, 2016)

[3] http://www.iswa.org/ (accessed April 10, 2016)

[4] http://ec.europa.eu/eurostat/documents/2995521/6757479/8-26032015-AP-EN.pdf/a2982b86-9d56-401c-8443-ec5b08e543cc (accessed April 10, 2016)

[5] http://www.atlas.d-waste.com/ (accessed April 12, 2016)

[6] Michaels, T., 2014, The 2014 ERC Directory of Waste-to-Energy Facilities, Energy Recovery Council.

[7] US EPA Archive Document, 2012, MSW Fact Sheet, *Municipality Solid Waste Generation, Recycling and Disposal in the United States: Facts and Figures for 2012.*

[8] http://www.worldbank.org/ (accessed April 3, 2016)

[9] http://ec.europa.eu/eurostat (accessed April 3, 2016)

[10] Themelis, N.J., Mussche, C., 2013, Municipal Solid Waste Management and Waste-to-Energy in the United States, China and Japan, 2nd International Academic Symposium on Enchanced Landfill Mining.

[11] Themelis, N. J., Barriga, M.E.D., Estevez, P., Velasco, M.G., 2013. Guidebook for the Application of Waste to Energy Technologies in Latin America and the Caribbean, Earth Engineering Center, Columbia University.

[12] Fernandez, I., 2013, Australia – Land of Opportunity for Waste to Energy & Recycling., Waste Management World.

[13] Laschon, E., 2016, *Contract inked for $400m Kwinana thermal waste facility in WA.*, ABC News.

[14] Cooper, J. 2011. Japan’s Waste Management Situation, Waste Management World.

[15] Ministry of the Environment, 2014, History and Current State of Waste Management in Japan., Ministry of Environment.

[16] http://www.econews.gr/2016/03/01/kina-apovlita-energeia-128799/ (accessed April 4, 2016)

[17] Themelis, N.J., Zhang, Z., 2010. WTE in China, Waste Management World.

[18] Allen, C., 2012, TAIWAN, *Community Action Leads Government Toward Zero Waste.*, GAIA (Global Alliance for Incinerator Alternatives)

[19] http://www.tradingeconomics.com/taiwan/gdp (accessed April 3, 2016)

[20] Ryu, C., Shin, D., 2013, Combined Heat and Power from Municipality Solid Waste: Current Status and Issues in South Korea., Energies.

[21] Themelis, N.J., Seo, Y., 2013, Current MSW Management and Waste-to-Energy Status in the Republic of Korea, Earth Engineering Center, Columbia University.

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A social survey (2016) on how the economic crisis affects peoples' attitudes towards energy and environmental subjects

P. Kosmopoulos*, A. Kantzioura, I. Kosmopoulos, K. Kleskas, A. M. Kosmopoulos

Laboratory of Environmental and Energy Design of Buildings and Settlements,
Democritus University of Thrace, Department of Environmental Engineering, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

This article presents a panhellenic social survey regarding Environmental subjects. It is a well-known fact that Greece is suffering from an Economic Crisis among other E.U. countries. This crisis coincides with the time that Greece is supposed to take measures for Environmental Protection in general, that should aim both at Energy Saving, and at gaining energy from Renewable and Alternative Sources. During the last decade, our Laboratory is conducting social surveys regarding people's attitudes towards the Environmental issues and the application of RES every two years. This specific research presented here is of special interest. It aims at the investigation of how peoples' attitudes and views towards the Environmental subjects and the use of RES. are affected by the Economic Crisis, and a rather dystopian general future. How serious and important are the environmental issues considered to be when people feel that their everyday life is threatened? This subject is approached through a panhellenic survey analyzing the data gathered by questionnaires.

Within a framework of an international economic crisis, Hellas has been the first of the European countries that has been badly affected. But at the same time, according to the E.U. Directives, Hellas has to conform with the regulations regarding the application and the use of Renewable Energy Sources.

It is very interesting to see how environmental matters are faced in general, regarding energy sources, fuels and related costs during this transitory period. But parallel to the above, Hellenic people have to face their household economics, their traditional attitudes towards their environment (both built and natural) and their dependence from imported fuels (oil and gas).

It is at least an intriguing subject to see how people cope with the above mentioned circumstances. Among other research projects our Laboratory, every two years, conducts a social research regarding the attitudes of Hellenic people towards R.E.S. (see Kosmopoulos 2002; 2004; 2006; 2008; 2011; 2013).

A large number of areas and cities have been covered, offering a satisfactory image of the subject. The conclusions of the research project, are very important describing peoples' attitudes towards environmental and R.E.S. matters during this critical period of the country.

Keywords: energy; Renewable and Alternative Sources; environment; social survey; economic crisis.

1. INTRODUCTION

Within a framework of an international economic crisis, Hellas has been the first of the European countries that has been badly affected. But at the same time, according to the E.U. Directives, Hellas has to conform with the regulations regarding the application and the use of renewable Energy Sources.

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The perspective of R.E.S. application covers a wide range of fields. The first level, according to the recent legislation, regards the application of R.E.S. and especially photovoltaics in buildings whether private or state, in order to achieve electricity production from the shelter of the buildings. The second level, regards the installation of larger units of P.V. systems in land properties. The third level, refers to the large scale installations, which aim at a national level of R.E.S. exploitation.

It is also interesting to see how environmental matters are faced in general, regarding energy sources, fuels and related costs during this transitory period.

The sensitivity of Hellenic people towards environmental matters is a well known fact: the traditional architecture, the antiquities, the natural environment and the related protective legislation, have established a concrete culture, which more or less, nowadays has to be denied. It is obvious that a new environmental aesthetics culture has to be shaped.

But parallel to the above, Hellenic people have to face their household economics, their traditional attitudes towards their environment (both built and natural) and their dependence from imported fuels (oil and gas).

It is at least an intriguing subject to see how people cope with the above mentioned circumstances.

Among other research projects our Laboratory, every two years, conducts a social research regarding the attitudes of Hellenic people towards R.E.S. (see Kosmopoulos 2002/2004/2006/2008/2011/2013) [1,2,3,4,5,6,7,8,9]. The increasing interest regarding the R.E.S. applications and their benefits, has been well shown during the past years, and also the increasing level of familiarity with the related subjects has also been shown. But this instance, with the official legislation on one hand pressing for the use of R.E.S., and the economic crisis on the other hand, the present social survey seemed to be at least intriguing.

2. ANALYSIS

2.1 The research project

The survey has been planed by the director and the staff of the laboratory of Environmental and Energy Efficient Design for Buildings and Settlements. An initial pilot study took place, some necessary corrections were made, and then the pan-Hellenic survey has been conducted. It lasted from October 2015 until February 2016. The survey has been carried out by members of the Laboratory and a large number of students and postgraduates that attend our lectures.

A large number of areas and cities have been covered, offering a satisfactory image of the subject.

As for the subjects among the citizens, there has been a random selection covering the whole area of each city and its suburbs, all age groups, and several occupation and educational level groups.

More over, two special groups have been investigated: a group of students of environmental engineering, and also a group of already qualified professionals that attend postgraduate courses regarding environmental design.

The questionnaires gathered, have been processed by the staff and the collaborators of our Laboratory. The task has been to extract easily understandable data, in order to help the authorities that might be interested to use the results of our survey.

The questionnaire is based upon the Guttman scale [10] but it has been adapted to the well approved and generally accepted 5 point Likert scale, in order to be comparable to all previous relative study [1,2,3,4,5,6,7,8,9].

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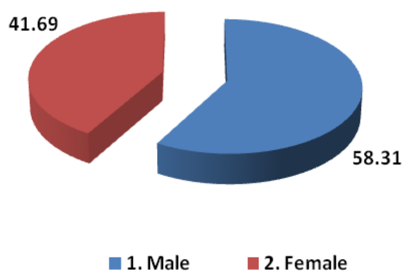
2.2 The survey

The research project, regarding the social attitudes towards the environmental subjects during this critical period, has lasted from 10/2015 to 2/2016, all over Hellas (and Cyprus) through the collection of questionnaires, and has covered the respective number of valid questionnaires:

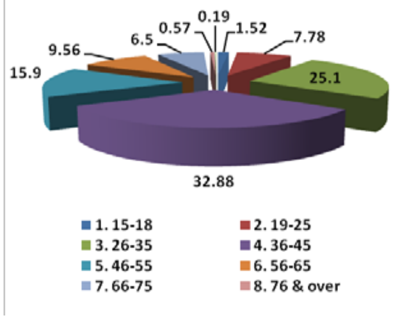
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ATHINA	274	KALAMATA	28	ORESTIADA	14
ALEXANDROUPOLI	34	KARDITSA	26	PATRA	43
AMYNTAIO	18	KASTORIA	33	PEIRAIAS	42
VEROIA	27	KATERINI	18	RETHYMNO	17
VOLOS	48	KERKYRA	22	RODOS	21
GIANITSA	19	KILKIS	18	SERRES	47
GREVENA	29	KOZANI	39	SPARTI	22
DIDYMOTEICHO	17	KOMOTINI	45	TRIKALA	17
DRAMA	34	KORINTHIA	28	TRIPOLI	11
EDESSA	29	KYPROS	48	TYRNAVOS	13
IGOUMENITSA	24	KOS	12	FLORINA	38
IRAKLEIO	42	LARISA	39	CHALKIDA	21
THESSALONIKI	185	LEFKADA	11	CHANIA	15
THIVA	27	MYTILINI	21		
IOANNINA	22	NAFPLIO	18		
TOTAL: 1667					

2.3 The social survey results:

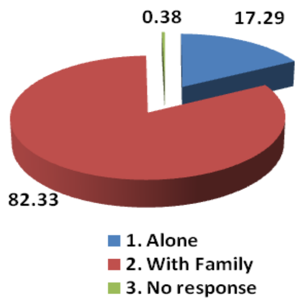
2. Sex



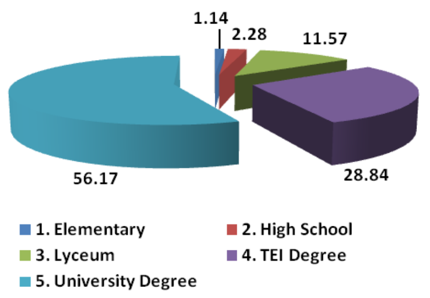
3. Age Groups



4. I live…

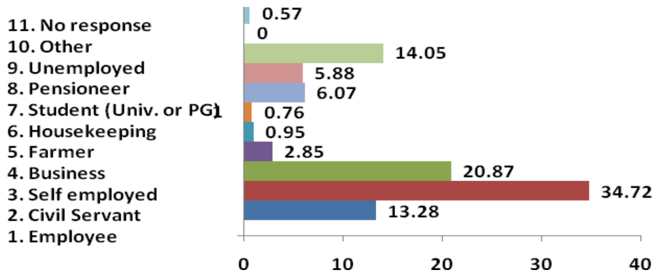


5. Educational level

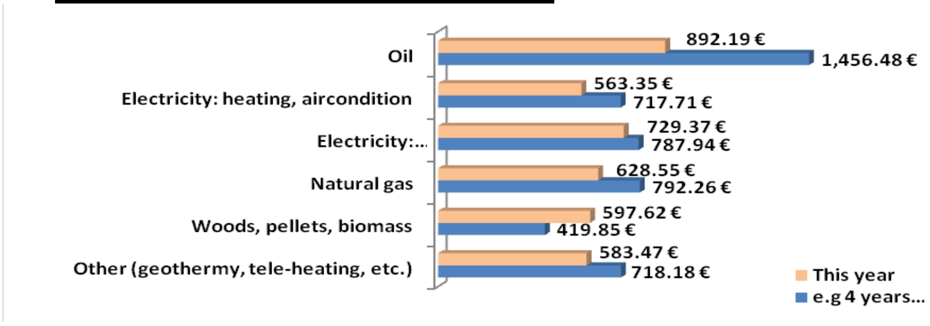


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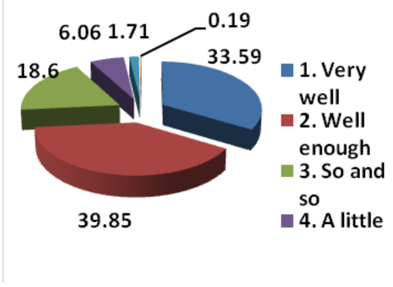
6. Occupation



7. How much money did you spent annually on various forms of energy, e.g four years ago and how much this year? (Averages)

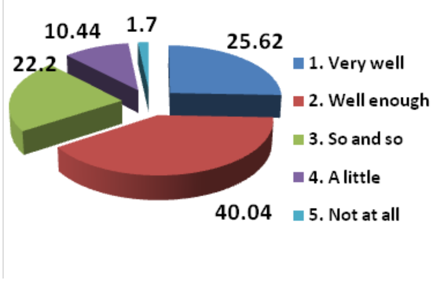


8. Do You know what Renewable Energy Sources are?

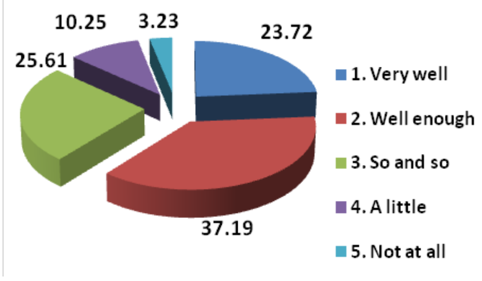


9. How well do you know about the following:

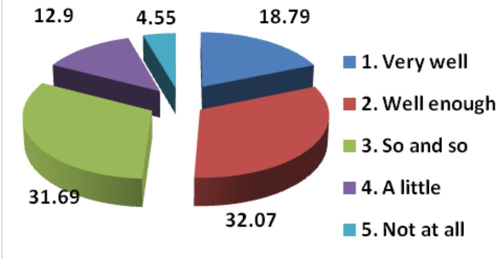
9.1 Photovoltaics in buildings:



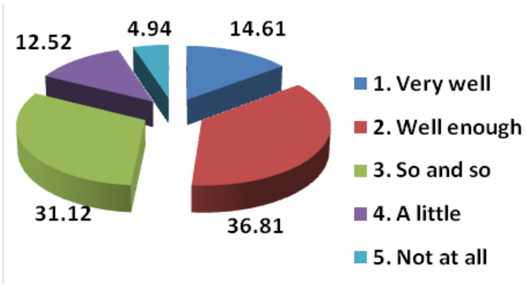
9.2 Photovoltaics in land properties:



9.3 Photovoltaic Parks:

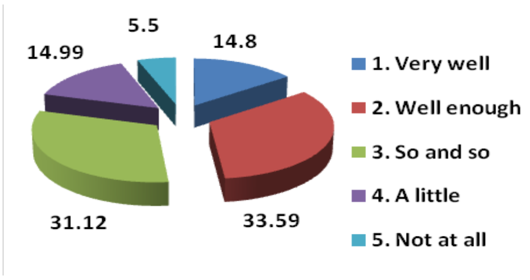


9.4 Wind Generators:

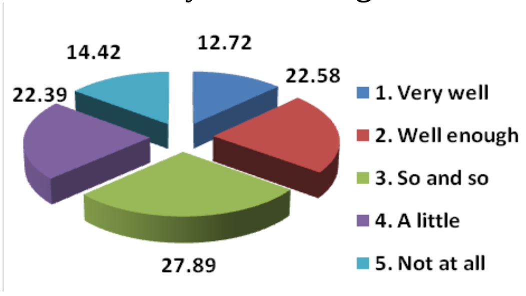


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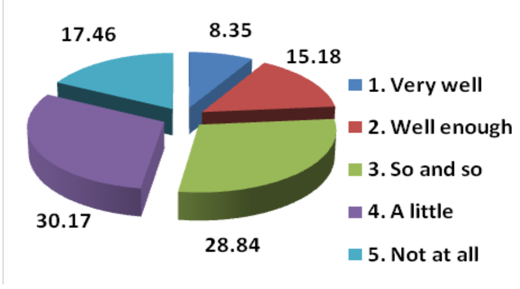
9.5 Wind Generators Parks:



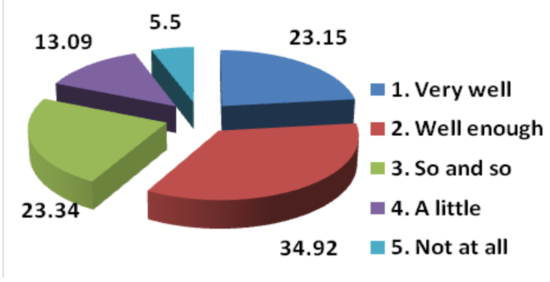
9.6 Geothermy for buildings:



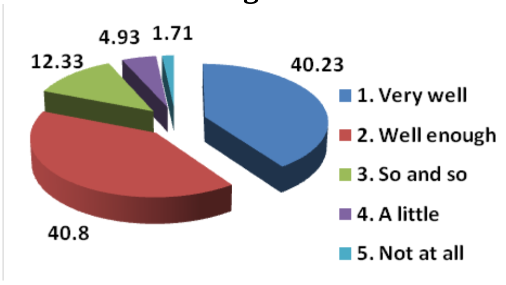
9.7 Geothermy for settlements:



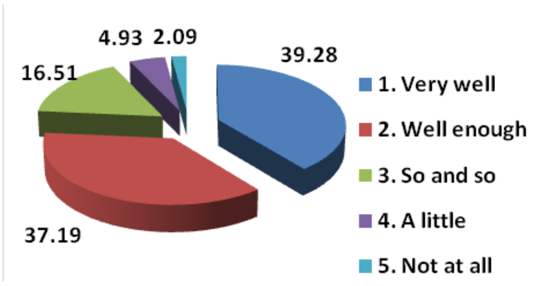
9.8 Biomass (wood blocks and pellets):



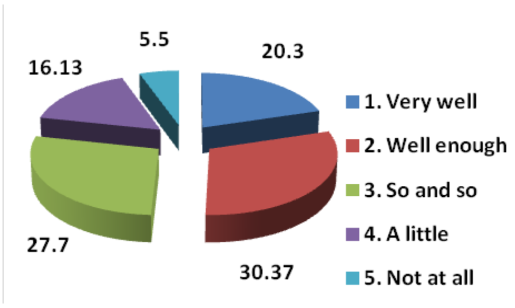
9.9 Double Glazing:



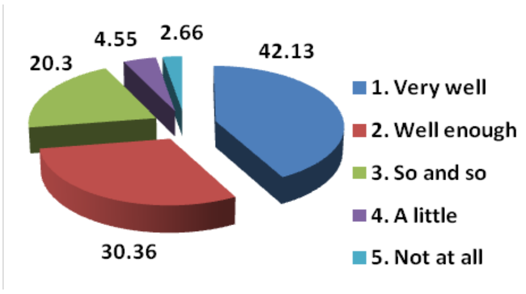
9.10 Insulation in walls:



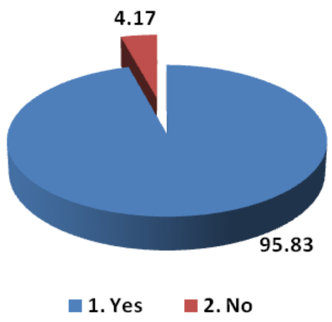
9.11 Glass House:



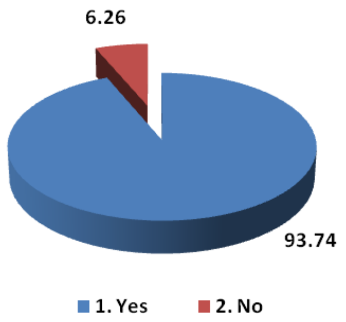
9.12 Fan:



<u>10. Do you know that all of the above can help the family income?</u>



<u>11. Do you know that all of the above can help our national economy to become independent from imported oil and natural gas?</u>

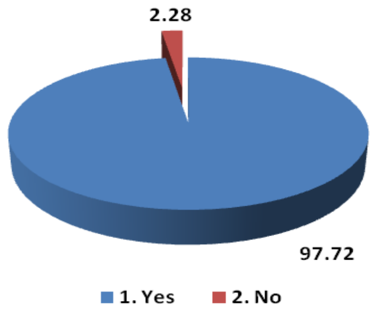


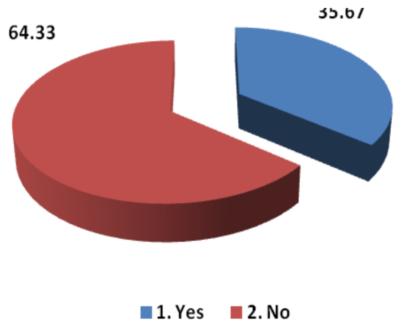
<u>12. Do you know that all of the above can</u>

<u>13. Do you already use any of the above?</u>

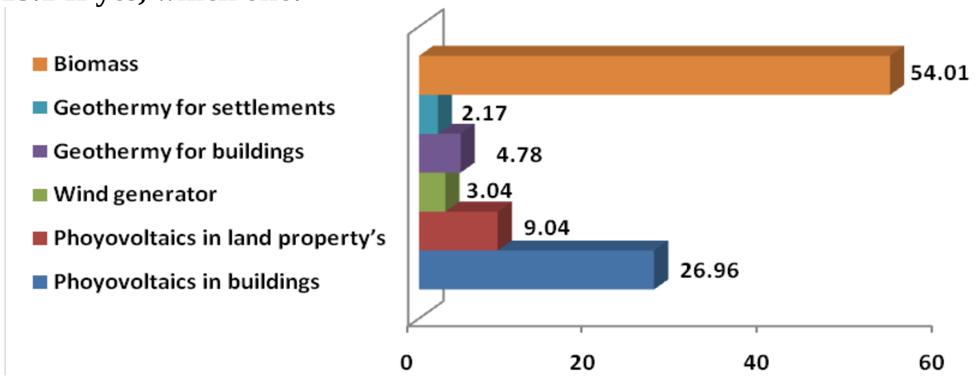
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help to reduce environment pollution?

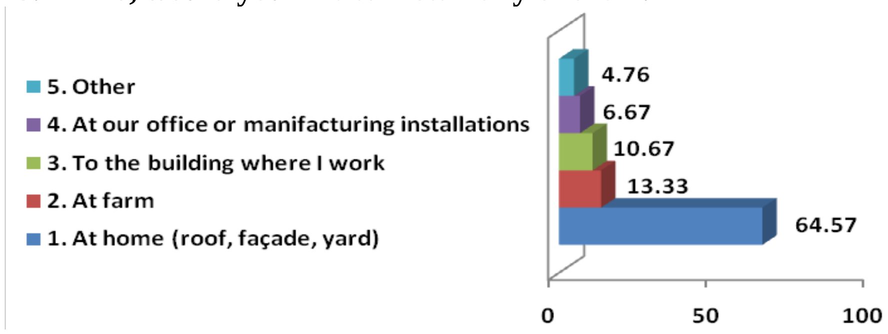




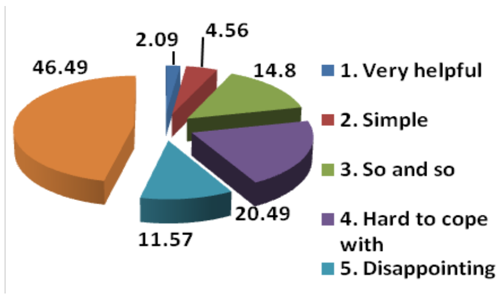
13.1 If yes, which one:



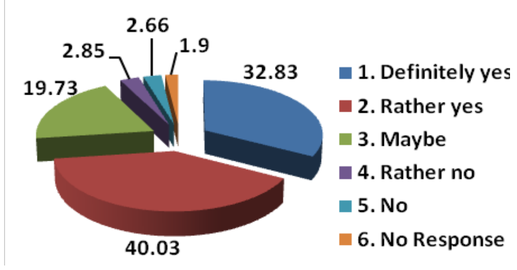
13.2 If no, would you like to install any of them:



14. If you have already attempted to do so, what is your comment on the necessary beaurocracy?



15. If you are reassured from the authorities that you will have definite economic gain, and a simple beaurocratic procedure, would you proceed to install any of the above?



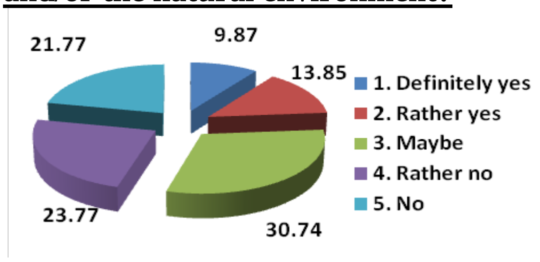
16. Do you think that the installation of

17. Would you accept a nuclear plant in our

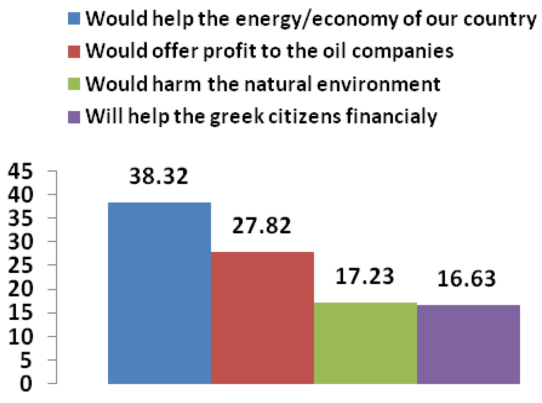
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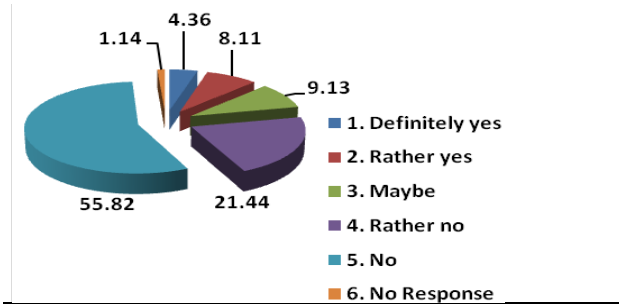
P.V.S and W.G.S insult/destroy the aesthetics/natural beauty of buildings and/or the natural environment?



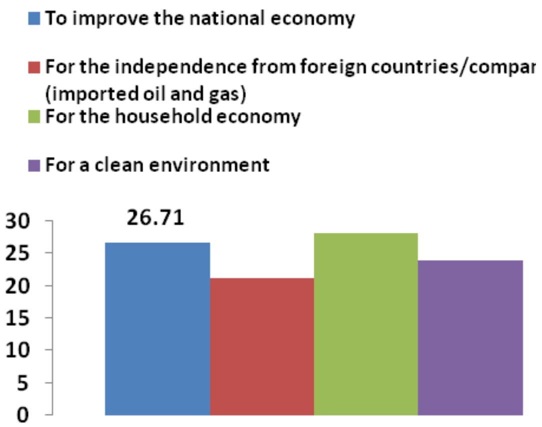
18. We have learned that there are fossil fuels in our country.
Do you think that their exploitation:



country?



19. Finally, would you wish to see a wide use of R.E.S. for the following reasons:



3. DISCUSION AND CONCLUSIONS

The number of the participants to this research, and the answers that have been gathered, permit us to point out several subjects of interest.

1. Both male and female, and also all age groups, have been covered satisfactorily.
2. The educational level and also the occupation of the participants, have also been covered satisfactorily.
3. The cognitive level regarding Renewable Energy Sources, seems to have scientifically improved regarding our previous relative surveys. Both the general questions regarding R.E.S. and the specific questions regarding partial subjects such as PV or WG or parks to mention some, seem to be “well enough” known by the public.
4. For example, to the question about PVs the “well enough” level from 30.7% in 2011, in this research, it has reached 42.27%. And regarding PV parks, the “well enough” from 25.20% has reached 31.02%.
5. Regarding WGs, from 25.72% in 2011 we find now 36.87%, and in WG parks, from 22.40% today it has reached 30.68%. In conclusion, the campaign by the media seems to be achieving its aim.
6. Geothermy does not seem to be well known, contrary to Biomass (wood blocks and pellets) that due to the high prices of oil and natural gas, seems to become popular (from 17.99% to 67.27%).
7. Regarding the economy point of view, several interesting remarks can be pointed out: Most people seem to have understood that R.E.S. can help both the family income and the national economy.

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8. Among the people that already use some of R.E.S., Photovoltaics and especially Biomass are ahead.
9. People who would like to install R.E.S., are interested to do so firstly at home, and then to a farm or land property.
10. A very important point that has been underlined, is that recently (August 2012) a new law has decreased the income from the installation of PVS, and it seems that this policy will continue. This legislation has a negative affect to the interest towards new installations of PVs.
11. Regarding bureaucracy, which seems to be a major problem in Greece, people seem to be disappointed, but in case the state should establish simple and clear rules and also some guaranteed economic gain for the citizens, R.E.S. applications should definitely increase.
12. Regarding personal attitudes about financial contribution to the R.E.S. application, an amazing 67.59%, despite the crisis, should willingly offer some money, depending upon each person's economic status.
13. Another interesting subject, is the change of the attitudes towards the aesthetics of the environment concerning the installation of R.E.S. all over the country. During two previous surveys (e.g. 2007, 2009) people seemed to be firmly against large scale installations, arguing about the natural environment preservation. Nowadays, most people seem more interested in installing R.E.S. in their property, since 80.14% declare not to be disturbed by the PVs and/or W.Gs.
14. Regarding the possibility of the construction a nuclear plant station in Greece, people point out the seismic activity of the area and the danger of severe pollution, and seem to be definitely against such an idea (84.1%)
15. Recently, it has been known that in Greece there are large amounts of fossil fuels. Of course people are not precisely informed, but anyway they consider that in case these fuels are exploited, firstly it would help the economy and the energy problem of this country, but also that it would offer profits to the (foreign) oil companies.
16. Finally it is interesting to see the general attitudes of the participants towards the wide use of R.E.S. firstly, for the protection of the environment, secondly for the improvement of the national economy, but also for the independence from imported fuels, and the less energy cost for each household, though this recently, seems to fade away.
17. Comparing now age groups with the answers gathered, younger people seem to be more familiar with PVs and WGs, more thoughtful about nuclear energy, more skeptical about the economics of the household, and more protective towards the environment.
18. Comparing the educational level of the participants with their views towards the environmental subjects, in brief we can observe that the higher the degree, the more they know about R.E.S., they are more reluctant to contribute financially to the state attempt for R.E.S. applications, they have faster been adapted to the idea of PVs and WGs around them, and that they point out as their main interest, the protection of the environment, though the use of R.E.S.

Concluding Remarks

1. Despite the economic crisis and a rather hard future, people seem to be well informed regarding the subject of R.E.S..
2. People are interested indeed for the protection of the environment, for the national economy, for the release from imported fuels, and finally for the personal/family economic profit from the application of R.E.S., but they are also disappointed from the new economic policy applied to R.E.S..

Acknowledgments

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References

[1] Kosmopoulos P., Kantzioura A., Kosmopoulos I, Kleskas K., Kosmopoulos A.M., 2014, A social survey on how the economic crisis affects peoples' attitudes towards the environmental subjects, *5th Environmental Congress of Macedonia*, 14-16 March, Thessaloniki

[2] Kosmopoulos P., A. Kantzioura, I. Kosmopoulos, K. Panopoulou, and K. Kleskas, 2011, A Social Survey on how the economic crisis affects peoples' attitudes towards the environmental subjects. *MESAEP*, 24-27 September, Ioannina.

[3] Kosmopoulos P., Bourikas L., Kantzioura A., Fragidou I.P., Georgiadou D., Zoras S., Pan-Hellenic Research on the R.E.S. application: A social survey of the cognitive level and the attitudes of the Greek people, *3rd International Conference Palenc*, 29 September-1 October, Rhodes Greece

[4] Kosmopoulos P., 2008, Research about RES applications and energy savings in Thessaloniki, 3rd Environmental Conference of Macedonia, 14 - 17 March 2008, Thessaloniki

[5] Kosmopoulos P., 2008, *Buildings, Energy and the Environment*, University Studio Press, Thessaloniki

[6] Kosmopoulos P., 2004, *Environmental Psychology*, University Studio Press, Thessaloniki

[7] Kosmopoulos P., Ioannou Th, 2005, Social attitudes about environmental Design, *I.C. PALENC*, Santorini, Greece

[8] Kosmopoulos P., Ioannou Th, 2005, Comparative evaluation of social attitudes in Greece and Cyprus, *13th I.S. MESAEP*, Thessaloniki

[9] Kosmopoulos P., 2005, National Research regarding attitudes about R.E.S. *13th I.S. MESAEP*, Thessaloniki

[10] Canter D., 1998, *Environmental Psychology*, Thessaloniki, University Studio Press.

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Environmental Enterpreneurship

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Review of the Eco-design proposed legislation in industrial furnaces/burners regarding energy consumption and the related greenhouse gas emissions

P. Papadatos*, C. S. Psomopoulos, G. Ioannidis

Department of Electrical Engineering, Piraeus University of Applied Sciences, 250,
Thivon & P. Ralli Street, 12244, Egaleo - Athens, Greece
*Corresponding author: Email: ppapadatos@windowslive.com

Abstract

Based on the Lot 4: Industrial and Laboratory Furnaces and Ovens – Tasks 1 – 7 Final Report of 2012, the European Commission's Working Document of 2014 for the Ecodesign Consultation Forum on industrial and laboratory furnaces and ovens, depicted the first draft measures and requirements for the product group, aiming specific energy savings and the related greenhouse gases emissions'(GHG) reduction. In this paper, the abovementioned studies' results regarding energy consumption and GHG emissions will be demonstrated. These draft calculations and predictions launch the discussions on the future measures, in order to conclude to the official Mandatory Regulation.

Keywords: Eco-design; energy consumption; European Union legislation; greenhouse gases emissions; industrial furnaces/burners

1. INTRODUCTION

Ecodesign legislation studies regarding industrial furnaces/burners have reached halfway. In 2005, the initial version of the Eco-design Directive for Energy-using Products (EuPs), was published. [1,2] In 2008, an amending Directive to the Eco-design Directive 2005/32/EC was adopted, while in 2009, the recast of this Eco-design Directive was drafted. The Eco-design Directive 2009/125/EC sets the framework to decide on policies directly affecting energy-related products in the 27 Member States. The first Working Plan of the Eco-design Directive adopted in 2008 listed the product groups which were considered as a priority for implementing measures in 2009-2011. The Commission prioritized ten product groups that have a volume of sales and trade of more than 200,000 units per year within the Community, along with significant environmental impact: High energy consumption, long operating time, related emissions and waste generation and other environmental impacts of materials used. However, these products have also a significant potential for improvement, such as high potential for energy savings and potential for other environmental improvements. This list included 'industrial and laboratory furnaces and ovens'. On this cause, a preparatory study was launched in 2010 resulting to a final report that was published in September 2012. Eventually, the European Commission's Working Document of 2014, presented the first indicative, draft, eco-design requirements/measures for discussion in the Consultation Forum, which consists of stakeholders, groups of experts, etc. (Figure 1)

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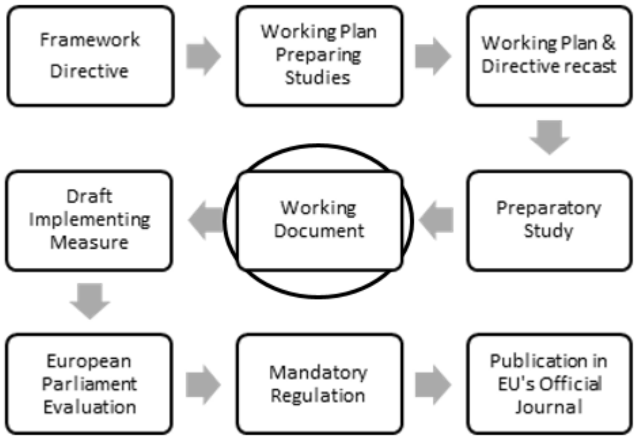


Figure 1: Environmental Legislation process so far, regarding Industrial Furnaces and Ovens product group [1]

The Eco-design Directive's target is to set the frame of the mandatory minimum requirements for each product group, leading to specific implementing measures for each product group after a certain procedure. There is a lot of research material regarding the European Commission's Eco Design Directives and its prioritized product groups that are set under investigation, especially the ones related to the domestic sector. But, regarding the 'industrial and laboratory furnaces and ovens' product group, although there is a complete study building on the Eco Design Directive, an absence of a summary concerning the industrial furnaces specifically can be observed. In this paper, this 'gap in knowledge' will be attempted to be covered. [1-10]

2. BASE CASES AND ENVIRONMENTAL IMPACTS

According to the EC's Working Document and the corresponding preparatory study, the current final energy consumption of all industrial and laboratory furnaces and ovens is 1650 TWh/year, i.e. almost the half of the overall EU industrial sectors' energy consumption. The ENTR Lot 4 preparatory study classifies furnaces depending to their size to laboratory (<120 litres), small and medium (120<capacity<10 tones for batch and 120<per day<20 tones for continuous) and finally, large and very large (>10 tones capacity for batch and >20 tones / day for continuous). It also categorizes the product group in 7 major base cases (BCs) as follows:

- BC1: Laboratory ovens and furnaces
- BC2: Medium size batch oven (electric/gas)
- BC3: Batch chamber furnace (electric/gas)
- BC4: Continuous oven (electric/gas)
- BC5: Continuous belt furnace (electric/gas)
- BC6: Large furnace (fossil fuel [gas])
- BC7: Very large oven (fossil fuel [gas])

The current paper focuses on the medium and large sized furnaces and oven products which consume approximately 1,646 TWh of energy per year and the 2-7 base cases.[1] For the better and more detailed comprehension of the above categories the next list was created, categorizing the products according to the fuel used for their operation [9,10]:

- BC2a: Medium size batch oven (electric)
- BC2b: Medium size batch oven (gas)
- BC3a: Batch chamber furnace (electric)
- BC3b: Batch chamber furnace (gas)
- BC4a: Continuous oven (electric)

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- BC4b: Continuous oven (gas)
- BC5a: Continuous belt furnace (electric)
- BC5b: Continuous belt furnace (gas)
- BC6: Large furnace (fossil fuel [gas])
- BC7: Very large oven (fossil fuel [gas])

The environmental impacts of each base case will be assessed in the next lines. The impact assessment was held by the Lot 4 study based on the MEEuP (EcoReport Unit Indicators) methodology for each life-cycle stage [9]:

a) Raw materials use and manufacturing (production phase)
b) Distribution phase
c) Use phase
d) End-of-life phase

In the ENTR Lot 4 study, European Union's 27 Member States total impacts were calculated with the multiplication of the environmental impacts of each base case by the number of this base case type of furnace/oven currently in stock in the Union. In this work, special focus will be given to the energy consumption and the GHG emissions impacts, which are also some of the most significant issues for the environment. These impacts are demonstrated per base case and in total, annually, in Table 1.

For the base cases 2-5 (medium size furnaces & ovens) there is a total primary energy consumption of 760.88 PJ/year, so approximately 211 TWh/year. There is also a Global Warming Potential (GWP) of 34 million tonnes CO_2 equivalent per year. According to the Lot 4 study, the electrical-powered furnaces/ovens demonstrate the largest environmental impacts during their use phase (due to electricity consumption). On the other hand, gas-powered furnaces/ovens demonstrate 5 major impacts during their use phase and 5 major impacts during the production of the materials phase. This difference probably exists due to the different materials used in calculations, regarding the production phase of furnaces and ovens.

For the base cases 6 and 7 (large size furnaces & ovens), there is approximately 5165 PJ/year, or ~ 1435 TWh/year (of a total of ~ 1650TWh/year, or 5935.07 PJ/year). The GWP impact of these two base cases is almost 287 million tonnes CO_2 equivalent per year. Pursuant to the Lot 4 study, the major environmental impact of these large-sized furnaces/ovens, is the energy consumption in the use phase, highlighting the specific products as the major energy consumer in the sector.

In conclusion, the energy consumption of the industrial furnaces and ovens sector in the European Union, corresponds to approximately 5935 PJ/year or 1650 TWh/year. However, this value includes energy consumed during the use phase but also the production and dispose phase of the products. The respective amount of the Global Warming Potential, is 321 million tonnes CO_2 equivalent per year.

At this point it should be mentioned that the connection between energy consumption and greenhouse gases emissions is not always obvious. For example, CO_2 emissions from coal combustion are greater than oil or gas combustion. Many furnaces use coal (i.e. cement production), others use gas and others electricity (for heating). Furnaces using gas, can be much more efficient than the ones using electricity – which is usually generated from fossil fuel sources.

In more detail, electricity generation efficiency, generally fluctuates between 30 to 40% either for coal or gas power generation. There are also transmission losses (2%) and the electric heating's so called "primary energy factor" ($1kWh_e$ generation corresponds to $\sim 2.5kWh_f$). On the other hand, (direct) fossil fuel-fired furnaces, seem to be less efficient, as long as the vented hot combustion gases are interpreted to heat loss. Nevertheless, heat losses are common in both cases, they just occur in different phases (generation for electricity, use phase for fossil fuels). [9]

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Table 1: Major environmental Impacts of the product group [9]

Annual Energy Consumption and GHG Emissions by furnaces/ovens in the EU											
Base Cases	BC 2a	BC 2b	BC 3a	BC 3b	BC 4a	BC 4b	BC 5a	BC 5b	BC 6	BC7	Total
Total Energy (PJ)	347	48.67	39.17	5.49	252.91	35.37	28.30	3.97	4952.74	212.45	5926
Electricity Consumption (PJ)	347	0.01	39.03	0	251.35	0.04	28.25	0	8.87	0.43	675
GHG in GWP100 (million tonnes of CO_2 eq.)	15	2.69	1.72	0.3	11.11	1.96	1.24	0.22	274.79	11.81	321

3. ENERGY CONSUMPTION AND GHG EMISSIONS ACCORDING TO ECO – SCENARIOS

The scenarios regarding eco-design measures implementation, met in the Lot 4 study are:

- the No action scenario (referred also as BaU - Business as Usual)
- the Policy recommendation scenario: implementation of minimum Energy Performance Standards in three Tiers (2014, 2018 and 2024)
- the LLCC (Least Life Cycle Cost scenario): implemented from 2014
- the BAT (Best Available Technologies scenario): implemented from 2014, expressing the maximum energy saving potential achievable

The 2014 European Commission's Working Document concludes in two major policy options for further investigation through Impact Assessment studies:

1. *Draft proposals for Ecodesign Implementing Measures relevant for Lot 4 furnaces and ovens, subdivided according to Base Case and*
2. *Regulating Lot 4 furnaces and ovens through the Industrial Emissions Directive (IED) sectoral BAT conclusions (higher chance of being more effective, through sectoral customisation) or the Horizontal Energy Efficiency BAT conclusions, via the same "ecodesign-style" provisions. This option would enhance IED by providing clearer energy consumption targets, but should not conflict with ETS and its "benchmarking" system.*

The 2nd Policy Option concerns the same issues as the 1st, but to be applied through the already existing legislation of the IED sectoral Best Available Technologies conclusions. [10-13] The proposed eco-design measures according to the EC's Working Document, are synoptically presented in Table 2.

The heat recovery option regards direct gas-fired base cases, the improved insulation option regards electricity and direct gas-fired base cases and the Optimized control of fuel/air ratio "λ" option regards indirect gas-fired base cases. Any specific limitations, exceptions and detailed implementation standards, are beyond the purposes of this paper, so they are intentionally ignored.

In 2014 Working Document's Annex E, the scenarios under investigation in terms of (the ongoing) Impact Assessment appraisal, were altered (compared to Lot 4) to the following:

- No action scenario
- Policy Options related scenarios (Table 3):

Table 2: Proposed Ecodesing measures according to European Commission's Working Document [10]

Heat Recovery				
Size of the process	*Temperature of the process*	*Minimum amount of heat recovery per specific time period for flue gas containing 3% oxygen*		
		2016 and onwards % recovered & reused	2019 and onwards % recovered & reused	2025 and onwards % recovered & reused
Medium	<1 000°C	-	≥25% (flue gas≤500°C)	≥35% (Flue gas≤350°C)
Large	<1 000°C	flue gas≤600°C	≥35% (flue gas ≤500°C)	≥50% (flue gas ≤350°C)
Medium	≥1 000°C	-	≥30% (flue gas ≤550°C)	≥40% (flue gas ≤400°C)
Large	≥1 000°C	A minimum of 40% heat recovery	≥40% (flue gas ≤500°C)	≥55% (flue gas ≤300°C)

Insulation (heat losses)							
Base Case	2	3	4	5	6 (>1000°C o.t.*)	6 (450°C to 1000°C o.t.)	7 (<450°C o.t.)
Mandatory Requirements (W/m^2 away from "hot-spots")	< 300	< 300	< 500	< 400	< 500	< 400	< 200

*o.t. : operating temperature

Maximum λ value		
Time Period	2016 and onwards	2019 and onwards
NG	1.25	1.15
LPG	1.25	1.15
Fuel Oil	Not Yet Determined	Not Yet Determined

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Table 3: The 2 main policy eco-design options according to the EC's 2014 Working Document Annex E [14]

Policy Option 1			Policy Option 2		
Ecodesign Measures (only for sales of new products)			BAT applied through the already existing legislation (IED, etc.) – implemented on existing stock and new sales		
3 scenarios			3 scenarios		
Mandatory Ecodesign Requirements (MER) scenario	Least Life Cycle Cost (LLCC) scenario – only for reference	BAT	Optimistic	Realistic	Pessimistic
3 Tiers – starting from 2016 (2020, 2026)	Hypothetically implemented from 2016		starts in 2016	starts in 2018	starts in 2022

It should be mentioned that, generally, in terms of energy consumption (and GHG emissions where data are available), the BAT and LLCC scenarios overlap, both in Lot 4 study and the Working Document draft predictions (ANNEX E). [9,14]

Pursuant to the ENTR Lot 4 study, in the case of the 'No action' scenario, the product group would require approximately 1648 TWh of primary energy, on 2035. Correspondingly, the 25 year period under investigation (2011 to 2035), a total of 41188 TWh primary energy would be consumed, with a relevant impact of 8025 million tonnes of CO_2 equivalent. Of these, Base case 6 (large fossil fuel furnaces), are responsible for the 86% of the total emissions and for the 83% of the total energy consumption.

On the other hand, the minimum proposed energy performance measures as defined in the same study, would result to 1482 TWh of primary energy required on 2035, while a total of 39664 TWh over the whole 25-year period would be consumed. The corresponding amount of GHG emissions would be 7725 million tonnes of CO_2 equivalent for the same period. Of these, Base case 6 (large fossil fuel furnaces), are responsible for the 85% of the total GHG emissions and for the 83% of the total energy consumption.

Finally, the BAT scenario, as expected, would lead to the less environmental impacts: 1436 TWh of primary energy would be required on 2035 and a total primary energy consumption of 38835 TWh over the 2011 to 2035 period. The greenhouse gases total emissions will be 7561 million tonnes of CO_2 equivalent. Of these, Base case 6 (large fossil fuel furnaces), are responsible for the 85% of the total emissions and for the 83% of the total energy consumption. [9]

As regards the initial and indicative - draft Lot 4 impact assessment's predictions concerning energy savings, they confirm the positive effect of potential eco-design measures in energy consumption reduction. More specifically, the MER scenario is expected to provide 10% energy savings on 2035 compared to the No Action Scenario for all base cases and the respective LLCC/BAT hypothetical scenario ~12.9% energy savings for all base cases (Policy 1, including base case 1 – approximately same energy consumption values on 2035 with Lot 4 study). The BAT under the IED, is expected to provide 19.2% energy savings on 2035 for every of its time-related versions (~1332 TWh final energy consumption on 2035), compared to the No Action scenario (Policy 2). 90 TWh/year of energy savings (of all base cases) seems achievable if the Best Available Technologies are implemented. No greenhouse gases emissions forecast was included in these early Impact Assessment indicative results. [10,14]

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It should also be noted, that the Working Document's Annex E draft results, refer to final energy consumption/savings for fossil-fueled furnaces and ovens, while for primary energy consumption/savings for electricity-powered products (the conversion assumption that 2.5 Primary Energy→Final Energy use is made: so, 1 electricity kWh (kWh_e) corresponds to 2.5 kWh (KWh_f) of coal, NG, etc. required, with an electricity generation conversion efficiency of 40%). [10,14]

4. CONCLUSIONS

The environmental legislation process and the corresponding technical studies regarding Ecodesign in industrial furnaces/ovens (and inevitably, the included to the product group definition equipment – such as burners), have a long way to go. The Impact Assessment's final results, including enriched data and analysis are eagerly expected. Nevertheless, the accomplished studies so far, indicate high potential for significant energy savings and greenhouse gases emissions mitigation.

References

[1] Papadatos, P., Psomopoulos, C.S., Ioannidis, G. C., 2015. Review of the Eco-design legislation in Industrial furnaces/burners. *Proceedings of the 5th International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2015) & SECOTOX Conference*, Mykonos island, Greece, June 14 to 18, 2015, (Oral Presentation).

[2] European Commission, 2005. Directive 2005/32/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 6 July 2005, establishing a framework for the setting of ecodesign requirements for energy-using products and amending Council Directive 92/42/EEC and Directives 96/57/EC and 2000/55/EC of the European Parliament and of the Council. [Online] Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF /?uri=CELEX:32005L0032&from=EN (accessed May 17, 2016).

[3] European Commission, 2009. DIRECTIVE 2009/125/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products (recast) (Text with EEA relevance). [Online] Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32009L0125&from=EN (accessed May 17, 2016).

[4] European Commission, 2010. DIRECTIVE 2010/30/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 May 2010 on the indication by labelling and standard product information of the consumption of energy and other resources by energy-related products (recast) (Text with EEA relevance).
[Online] Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:153:0001:0012: en: PDF (accessed May 17, 2016).

[5] Ökopol Institut für Ökologie und Politik GmbH. Overview Ecodesign. [Online] Available from: http://www.eup-network.de/product-groups/overview-ecodesign/ (accessed May 17, 2016).

[6] Psomopoulos, C.S., Avramikos, I., Hermmann, C. Saraev, A., 2007. Study for preparing the first Working Plan of the Ecodesign Directive, Report for tender No: ENTR/06/026. [Online] Available from:
https://www.researchgate.net/profile/Constantinos_Psomopoulos/publications (accessed May 17, 2016).

[7] European Commission, 2008. COMMUNICATION FROM THE COMMISSION TO THE COUNCIL AND THE EUROPEAN PARLIAMENT, Establishment of the working plan for 2009-2011 under the Ecodesign Directive. (COM 2008 660). Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2008:0660: FIN: en:PDFpp.4-6 (4), ANNEX I (accessed May 17, 2016).

[8] Irrek, W., Barthel, C., Jepsen D., Reintjes, N., 2010. Ecodesign Directive Executive Summary, Summary report on Task 14 within the framework of the „Material Efficiency and Resource Conservation" (MaRess) Project. [Online] Available from: http://ressourcen.wupperinst.org/downloads/MaRess_AP14_6_ExecSummary.pdf (accessed May 17, 2016).

[9] Goodman, P., Robertson, C., Skarstein, A., Lyons, L., Pahal, S., 2012. Sustainable Industrial Policy – Building on the Eco-design Directive – Energy-Using Products Group Analysis / 2. Lot 4: Industrial and Laboratory Furnaces and Ovens –Tasks 1 – 7 Final Report. [Online] (ENTR Lot 4 Final Report). Available from: http://www.eceee.org/ecodesign/products/Industrial_ovens/043122753%20ENTR%20Lot%204%20Final%20Rep ort%20v6.pdf (accessed May 17, 2016).

[10] European Commission, 2014. WORKING DOCUMENT FOR THE ECODESIGN CONSULTATION FORUM ON INDUSTRIAL AND LABORATORY FURNACES AND OVENS (ENTR LOT 4), 16 MAY 2014 (ENTR/B1/mjb/Lot 4). [Online] Available from: https://www.ebpg.bam.de/de/ebpg_medien/entr4/404_wd_2014-05.pdf (accessed May 17, 2016).

ISBN: 978-960-6865-94-7

[11] European Commission, 2010. DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) (Text with EEA relevance). *Official Journal of the European Union, 17.12.2010*

[12] European Commission, Official Website. JOINT RESEARCH CENTRE. Institute for Prospective Technological Studies (IPTS). Reference Documents. Best Available Techniques Reference Document (BREFs). [Online] Available through: http://eippcb.jrc.ec.europa.eu/reference/ (accessed May 17, 2016).

[13] European Commission, 2003. DIRECTIVE 2003/87/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 13 October 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC (Text with EEA relevance). *Official Journal of the European Union, 25.10.2003.*

[14] European Commission, 2014. ANNEX E OF THE WORKING DOCUMENT FOR THE ECODESIGN CONSULTATION FORUM ON INDUSTRIAL AND LABORATORY FURNACES AND OVENS (ENTR LOT 4), 16 MAY 2014: INITIAL INDICATIVE DRAFT IMPACT ASSESSMENT ENERGY SAVINGS ACCORDING TO MODELLED POLICY OPTIONS AND FURNACE/ OVEN BASE CASES. [Online] Available through (Swedish Energy Agency): https://www.energimyndigheten.se/globalassets/ energieffektivisering/produkter-med-krav/ugnar-industriella-och-laboratorie/annex_e_policy_options_final.pdf (accessed May 17, 2016).

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Sulfogrow®: A new type of plant biostimulant?

S. Chorianopoulou[1], A. Venieraki[2], F. Maniou[1], H. Mavrogiannis[3], D. Benardos[3], P. Katinakis[2], D. L. Bouranis[1*]

[1] Plant Physiology Laboratory, Crop Science Department, Agricultural University of Athens, Iera Odos 75, 118 55 Athens, Greece.
[2] General and Agricultural Microbiology Laboratory, Crop Science Department, Agricultural University of Athens, Iera Odos 75, 118 55 Athens, Greece.
[3] Sulphur Hellas S.A., Leoforos Athinon 142, 104 42 Athens, Greece.
*Corresponding author: Email: bouranis@aua.gr

Abstract

Elemental sulfur (S^o) at a rate of 2% (w/w) has been attached successfully onto the surface of the beads of various commercial fertilizers (F) via a binder (B) by Sulfur Hellas S.A., thus creating a family of such products under the commercial name "Sulfogrow®" (FBS^o). The application of fertilizers of the FBS^o type to commercial crops of durum wheat and maize cultivated in calcareous soils so far have shown a significant enhancement of dry mass accumulation per plant and increased accumulations of nutrients in the aerial part, including the immobile ones in the soil. So is a well-known soil conditioner that needs the action of microorganisms for conversion into sulfates, i.e. the suitable form for S uptake by the plants. Moreover, our data revealed a prolonged enhancement of plant growth, a fact that is not justified by the amount of S^o incorporated in the soil with the application rate of FBS^o. According to the European Biostimulants Industry Commission "biostimulants operate through different mechanisms than fertilizers, regardless of the presence of nutrients in the products", therefore products with some nutrients can be included, provided that the effect on plant growth is not through direct fertilization. "Sulfogrow®" seems to fall into this category. In this contribution, we explore the sulfatase producing microbial population dynamics in the rhizosphere of a commercial wheat crop grown on a calcareous soil fertilized with FBS^o vs the corresponding commercial fertilizer F, in an attempt to assess the potential of FBS^o as biostimulant and to support a working hypothesis toward explaining its efficacy.

Keywords: elemental sulfur; plant biostimulants; coated fertilizers; wheat; sulfatases

1. INTRODUCTION

Elemental sulfur (S^o) is a well-known soil conditioner that needs the action of microorganisms for conversion into sulfates, i.e. the suitable form for S uptake by the plants. S^o oxidation is a biological process and as such is strongly influenced by factors that directly affect microbial activity. However, its oxidation to plant available sulfate is rather unpredictable, and therefore, the use of S^o towards alleviation of widespread S deficiencies in agricultural soils is mostly limited [1]. Oxidation is favoured by the fine particle size, whereas abundant populations of heterotrophic bacteria and fungi are capable of oxidizing S^o.

S^o as powder has been succesfully attached onto the surface of the beads of various commercial fertilizers (F), via a binder (B), by Sulfur Hellas S.A. at a rate of 2% (w/w), under the commercial name "Sulfogrow®" (FBS^o). So far, such S^o-containing fertilizers have been applied to commercial crops of maize and durum wheat cultivated in calcareous soils, revealing (1) a significant enhancement of dry mass accumulation per plant, (2) increased accumulations of nutrients in the

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aerial part, including the immobile ones in the soil, and (3) a prolonged enhancement of plant growth [2]. The last effect, especially, is not justified by the amount of S^o incorporated in the soil with the application rate of FBS^o, i.e. 2% S^o w/w. This fact raises the question whether the incorporated minor amount of S^o in the "Sulfogrow®" product also acts directly or indirectly as a plant biostimulant, raising a challenge as well; it is clear that microorganisms are involved in the oxidation process, but, so far, the process and its product has been highlighted, while it looks like it can be more than that. For example, some of these microbial populations could act as plant growth promoting microorganisms [3,4,5].

Plant biostimulants (PBs) include a variety of substances and microorganisms that enhance plant growth, therefore the concept and the definition of PBs is still evolving.The European Biostimulants Industry Council has defined PBs as follows: "PBs contain substance(s) and/or microorganisms whose function when applied to plants or the rhizosphere is to stimulate natural processes to enhance/benefit nutrient uptake, nutrient efficiency, tolerance to abiotic stress, and crop quality. Biostimulants have no direct action against pests, and therefore do not fall within the regulatory framework of pestisides". According to the European Biostimulants Industry Commission "biostimulants operate through different mechanisms than fertilisers, regardless of the presence of nutrients in the products". Therefore products with some nutrients can be included, provided that the effect on plant growth is not through direct fertilization. Sulfogrow® seems to fall into this category [6,7].

In this contribution, we focus on the sulfatase producing microbial population dynamics in the rhizosphere of a commercial wheat crop grown on a calcareous soil fertilized with FBS^o vs the corresponding commercial fertilizer F, in an attempt to assess the potential of FBS^0 as biostimulant and to support a working hypothesis toward explaining its efficacy. Arylsulfatase (ARS; arylsulfate sulfohydrolase; EC 3.1.6.1) belongs to the sulfatase family that hydrolyzes sulfate esters to sulfates, thus being the key enzyme of soil organic-S mineralization [8]. ARS has been isolated and widely studied from many microorganisms [9,10,11]. Soil sulfatases are principally microbial in origin. Sulfate esters are the most prevalent form of S in agricultural soils [12]. This labile organic pool has been found to be quickly available to plants after soil microbial transformations [13]; however, S deficiencies have been noted in some agricultural soils at the beginning of the growing season, due to either leaching of sulfates during the winter [14] or limited S mineralization in the soil.

Based on the above, the dynamics of population density, structure, and diversity of functional soil bacterial communities implicated in the mineralization of sulfate ester compounds in field-grown wheat following application of FBS^o fertilizer was monitored. The arylsulfatase-producing bacterial community (ARS-BC) was followed in the rhizospheric soil of field-grown wheat treated with FBS^o in comparison with rhizospheric soil of field-grown wheat that received the corresponding conventional fertilization (F). Samples were collected during the vegetative growth and the density, structure, and diversity of ARS-BC were investigated by applying a culture-dependent approach utilizing a M9 minimal medium in combination with the blue color production method using X-sulf, a chromogenic substrate that reports on bacteria mineralizing this sulfate ester with the appearance of a blue color [15]. The NA rich medium (Peptone 0.5%, Nutrient Broth 0.3%, Agar 1,5%) was also used for comparison. The total numbers of colonies (both blue and white ones) grown on NA rich medium against the M9 mininal X-sulf enriched medium were determined. Then, the percentage of blue colonies was calculated.

2. MATERIALS AND METHODS

A durum wheat (*Triticum durum*, cv SIMETO) commercial crop was established in Arma location at Viotia county, Greece, in an area of 1.7 ha with calcareous soil. Sowing day and initial fertilizer application took place in November 24, 2015 (d0). The field was divided into two parts; one of

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them was subject of control F-treatment, according to the local agricultural practices (control crop), whilst the other one received the corresponding FBS^0-treatment (FBS^0-treated crop). At d0, the control crop was fertilized with a commercial 16-20-0 fertilizer at a rate of 275 kg ha^{-1}. At the same day, the FBS^0-treated crop received the equivalent fertilization with the corresponding “Sulfogrow” 16-20-0 commercial fertilizer at the same rate, carrying 2% S^0 (i.e. 280.5 kg ha^{-1}). At d100 and d109 after sowing, additional fertilization with commercial 40-0-0 fertilizer (in control crop) or its “Sulfogrow” 40-0-0 version (in FBS^o-treated crop) took place at the rate of 360 and 367.2 kg ha^{-1} in total, respectively. At d122 after sowing, herbicide application took place at the rate of 50 ml $acre^{-1}$ (PACIFICA). Both crops received no irrigation. Each crop was divided into five plots and sampling took place separately in each one of them. A number of plants were collected with their root system and the surrounding soil by means of a shovel.

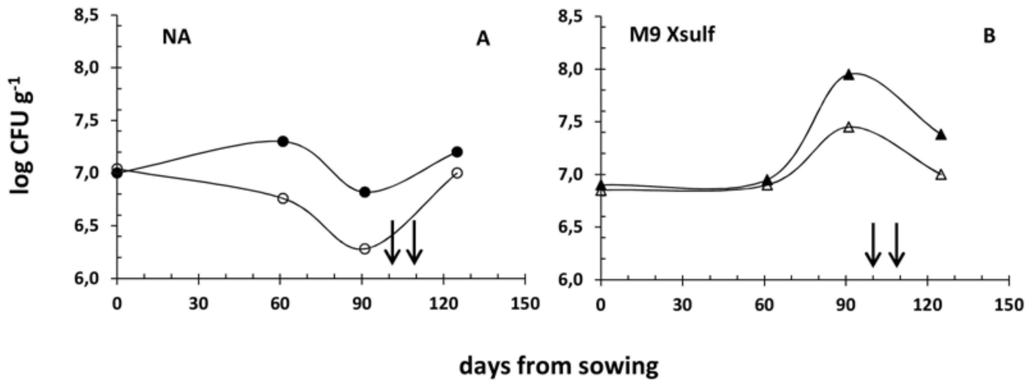


Figure 1. Time course of log CFU g^{-1} values in rhizospheric soil collected from durum wheat crop that received either conventional fertilization (control crop, C; empty symbol) or fertilization with the corresponding “Sulfogrow” fertilizer (FBS^0-treated crop; full symbol). Symbols (•) and (▲) indicate the use of nutrient agar medium (NA) or M9 minimal medium containing X-sulf respectively. Arrows indicate the timing of the additional fertilization.

Rhizosphere soil (5 g) was placed on an orbital shaker at 120 rpm for 30 min in 50 ml of phosphate buffer PBS at pH 7.2. The diluted suspensions were spread on the modified M9 mineral minimal medium containing the ARS chromogenic substrate, 5-bromo-4-chloro-3-indolyl sulfate (X-Sulf, Sigma), as sole sulfur source (X-sulf, Sigma, France). The blue colonies (expressing ARS activity) were counted after four days of incubation at 28°C and expressed as log CFU g^{-1} dry soil. Blue colonies were randomly picked from plates corresponding to the 10^{-3} dilution. Isolates were sub-cultivated three times on M9 minimal medium containing X-sulf for purification. Purified bacterial strains were stored frozen at -80°C in the presence of 12.5% glycerol.

3. RESULTS AND DISCUSSION

The time-course of colony forming units (log CFU g^{-1} values) in NA (Figure 1A), were progressively reduced in the control crop during the first three months, while the additional fertilization resulted in an increase back to the initial level (7.00). The corresponding time-course of FBS^0-treated crop increased significantly above the initial level at d61 and it returned to it 30 days later. Interestingly, the additional fertilization caused the same response pattern as in control, i.e. a significant increase nearly to the level of d61.

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Time-course of log CFU g^{-1} values in M9 minimal medium enriched with X-sulf (Figure 1B) were at the level of 6.9 for the first two months regardless of the treatment; thereafter the level significantly increased in both treatments. FBS^0-treated crop presented significantly higher values than that of control. After the additional fertilization both treatments presented a decline, with the FBS^0-treated crop keeping on providing significantly higher value.

The mean values of ARS-BC density on M9 minimal medium plates containing X-sulf (at 10^{-3} dilution), visualized by the blue colour resulting from the cleavage of the chromogenic substrate (Figure 2), were significantly greater in the FBS^0-treated wheat rhizospheric soil, as the percentage of the blue colonies was significantly higher in the FBS^0-treated wheat rhizospheric soil at each sampling.

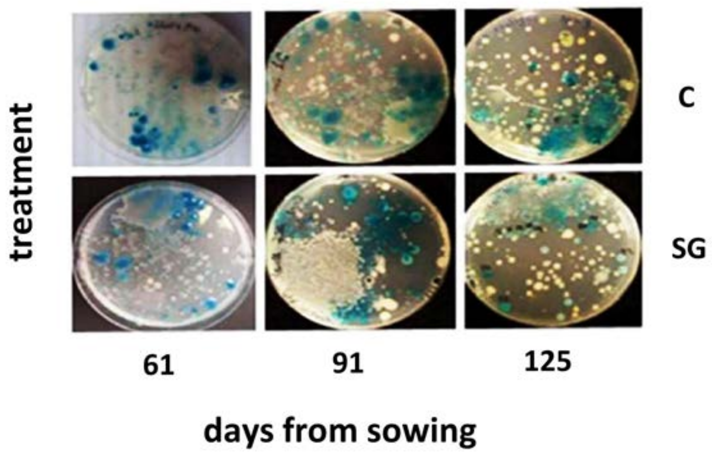


Figure 2. White and blue colonies developed on M9 minimal medium plates containing X-sulf (10^{-3} dilution). The blue ones were expressing ARS activity, which fluctuated with time.

At d61 in the rhizospheric soil of the FBS^0-treated crop, the blue colonies were 40% of the total ones, while at d91 it redused to 20% as opposed to 5% of the control crop. The additional fertilization increased the appearance of the blue colonies in both treatments, with a higher response of the FBS^0 treatment (Figure 3).

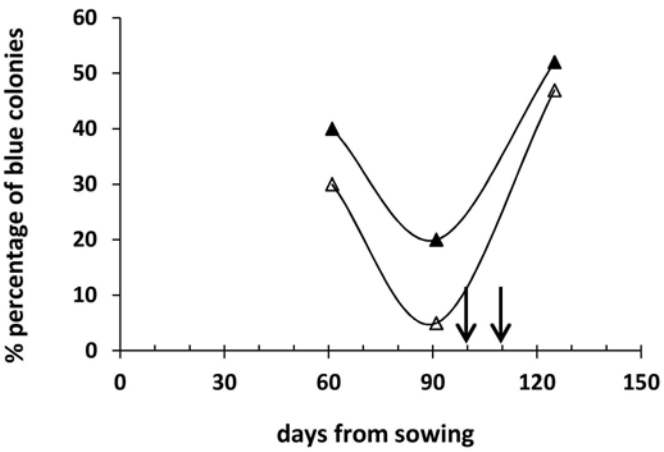


Figure 3. Time course of the percentage of blue colonies on the plates of Figure 2. Full symbol: blue colonies from the rhizospheric soil samples collected from the FBS^0-treated crop, i.e. the crop fertilized with the “Sulfogrow” fertilizer FBS^o. Empty symbol: the corresponding blue colonies from the rhizospheric soil samples of the control crop.

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Among the ARS-BC, more than four different taxa identified by means of classical microbiological methods. Among them, *Actinobacteria* and *Pseudomonas* were significantly present in the examined wheat rhizosphere soil. Fungal communities the rhizosphere soils of field-grown wheat treated with FBS^o in comparison with control field were also determined. All of the fungal isolates that displayed ARS activity were found to belong to *Ascomycotina*, a phylum preponderant in soils and especially in the rhizosphere.

Different bacterial strains have been characterized for their capacity to hydrolyze sulfate esters via the ARS activity [17]. S cycling is driven by the quantity and quality of the available carbon rather than total organic C [16], while the majority of the bacterial ARS activities are repressed in medium containing sulfates as a S source, but are expressed in media containing only organic S forms [18,19]. These results imply that the ARS activity is involved in scavenging organic S from the environment.

4. CONCLUSIONS

The 2% (w/w) of S^o encorporated into the used commercial fertilizer promoted the activity of the sulfatase producing microbial populations in the rhizosphere of the studied commercial wheat crop grown on calcareous soil. Therefore, the amount of S^o provided with the fertilizer significantly enhanced the mobilization of the labile pool of sulfate esters in the organic matter of the soil. This trait constitutes a part of the mode of action of “Sulfogrow” and suggests that this type of fertilizer can also function as a plant biostimulant.

References

[1] Germida, J.J., Jansen, H.H., 1993. Factors affecting the oxidation of elemental sulfur in soils. *Fertilizer Research*, **35**, 101-114.

[2] Chorianopoulou, S.N., Saridis, G.I., Sigalas, P., Margetis, M., Benardos, D., Mavrogiannis, H., Bouranis, D.L., 2015. Enhancing plant nutrition via S^0-based rhizosphere engineering: The application of a new generation of S^0-coated fertilizer to durum wheat crop. 10th Jubilee Plant Sulfur Workshop: Fundamental, Environmental and Agricultural Aspects, Goslar, Germany, 42.

[3] Gahan, J., Schmalenberger, A., 2014. The role of bacteria and mycorrhza in plant sulfur supply. *Frontiers in Plant Science*, **5**, 723.

[4] Kertesz, M.A., Mirleau, P., 2004. The role of microbes in plant sulfur supply. *Journal of Experimental Botany*, **55**, 1939-1945.

[5] Kertesz, M.A., Fellows, E., Schmalenberger, A., 2007. Rhizobacteria and plant sulfur supply. *Advances in Applied Microbiology*, **62**, 235-268.

[6] Calvo, P., Nelson, L., Kloepper, J.W., 2014. Agricultural uses of plant biostimulants. *Plant and Soil*, **383**, 3-41.

[7] du Jardin, P., 2014. Plant biostimulants: Definition, concept, main categories and regulation. *Scientia Horticulturae*, **196**, 3-14.

[8] Tabatabai, M.A., Bremner, J.M., 1970. Arylsulphatase activity in soils. Factors affecting arylsulfatase activity. *Soil Society America Proceedings*, **34**, 225–229.

[9] Beil, S., Kehrli, H., James, P., Staudenmann, W., Cook, A.M., Leisinger, T., Kertesz, M.A., 1995. Purification and characterization of the arylsulfatase synthesized by Pseudomonas aeruginosa PAO1 during growth in sulphate free medium and cloning of the arylsulfatase gene (atsA). *European Journal of Biochemistry*, **229**, 385–394.

[10] Parenti, G., Meroni, G., Ballabio, A., 1997. The sulfatase gene family. *Current Opinion in Genetics & Development*, **7**, 386–391.

[11] Goodwin, P.H., Li, J., Jin, S., 2000. Evidence for sulfate derepression of an arylsulfatase gene of Colletotrichum gloeosporioides f. sp. malvae during infection of round-leaved mallow, *Malva pusilla*. *Physiology and Molecular Plant Pathology*, **57**, 169–176.

[12] Bettany, J.R., Stewart, J.W.B., 1982. Dynamics of soil organic phosphorus and sulfur. 12th International Congress of Soil Science, New Delhi, India, 14.

[13] McLaren, R.G., Kerr, J.I., Swift, R.S., 1985. Sulphur transformations in soils using sulphur-35 labelling. *Soil Biochemistry*, **17**, 73–79.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[14] Suhardi, B.,1992. Importance du soufre organique du sol dans la nutrition soufre´e duble´ (Triticum aestivum L.). Thèse de Doctorat, INPL, Nancy, France, 147.
[15] Wyss, C., 1989. Campylobacter-Wolinella group organisms are the only oral bacteria that form arylsulfatase-active colonies on a synthetic indicator medium. *Infection and Immunity*, **57**, 1380–1383.
[16] DeLuca, T.H., Keeney, D.R., 1994. Soluble carbon and nitrogen pools of prairie and cultivated soils: seasonal variation. *Soil Science Society of America Journal*, **58**, 835–840.
[17] Kertesz, M.A., 1999. Riding the sulfur cycle metabolism of sulfonates and sulfates esters in Gram-negative bacteria. *FEMS Microbiology Reviews*, **24**, 135–175.
[18] Dodgson, K.S., White, G.F., Fitzgerald, J.W., 1982. Sulfatases of Microbial Origin. CRC Press, Boca Raton, FL.
[19] Kertesz, M.A., Leisinger, T., Cook, A.M., 1993. Protein induced by sulfate limitation in *Escherichia coli*, *Pseudomonas putida* and *Staphylococcus aureus*. *The Journal of Bacteriology*, **175**, 1187–1190.

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Green biotransformations catalyzed by enzyme–inorganic hybrid nanoflowers in environmentally friendly ionic solvents

A. Papadopoulou[1], A. Tzani[2], A. C. Polydera[1], P. Katapodis[1], A. Detsi[2], E. Voutsas[2], H. Stamatis[1*]

[1] Department of Biological Applications & Technologies, Laboratory of Biotechnology, University of Ioannina, University Campus, 45110, Ioannina, Greece.
[2] School of Chemical Engineering, National Technical University of Athens, Heroon Polytechniou 9, Zografou Campus, 15780, Athens, Greece.
*Corresponding author: Email: hstamati@uoi.gr

Abstract

Third generation ionic liquids and deep-eutectic-solvents formed by a mixture of non-toxic, biodegradable and inexpensive compounds represent a promising alternative option to organic solvents in various processes. In the present study, we have investigated the ability of lipase-nanoflowers to catalyze hydrolytic and synthetic reactions in environmentally friendly ionic liquids based on various hydroxyl ammonium cations and formic acid anion, as well as in choline chloride and ethyl ammonium chloride based deep eutectic solvents (DES). The hydrolytic and synthetic activity of the immobilized enzyme, as well as its stability and reusability, strongly depend on the nature of the ionic solvents used. In choline chloride-based DES, the activity and especially the stability of the biocatalyst are significantly increased compared to those observed in buffer, indicating the potential application of these novel solvents as green media for biocatalyzed processes of industrial interest.

Keywords: biocatalysis; green solvents; ionic liquids; deep eutectic solvents;

1. INTRODUCTION

The serious environmental impact of processes derived from chemical and pharmaceutical industries have raised the necessity for sustainable processes and environmentally friendly reaction systems. The field of biocatalysis is considered as a green technology that offers many benefits in this respect [1]. Enzymatic reactions, unlike conventional chemical synthesis, could be developed in one synthetic step in mild conditions with high selectivity towards the desired product, minimizing therefore the energy consumption and waste production [2].

On the other hand. ionic liquids (ILs) and deep eutectic solvents (DES), based on their unique properties, have emerged as a green alternative to organic solvents in biocatalysis and biotransformations [3]. ILs are mixtures of anions and cations that remain liquid at room temperature, while DES are natural mixtures of salts (e.g. choline chloride) and uncharged hydrogen-bond donors (HBD) (such as urea, carboxylic acids, or polyols). These mediaom have negligible vapour pressure, high chemical and thermal stability and the ability to dissolve various compounds. The recently developed third generation ILs comprise of biodegradable and readily available components of low toxicity such as natural bases and acids, amino acids and sugars. Together with DES, which can be easily synthesized from cheap and biodegradable compounds, both of these media represent promising solvents for enzyme-catalyzed reactions [4].

However, the use of enzymes in such solvents could have a negative effect on their activity and stability since they could interact with the water molecules around the protein surface or with the

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protein itself, reducing the activity or even inactivating the enzyme [5]. Different methods have been developed in order to eliminate these negative effects including the immobilization of enzymes in solid supports. Moreover, immobilized enzymes could be easily recovered and reused facilitating the biocatalytic prosess [6].

Over the last decades, enzyme immobilization on nanostructured materials have attracted the scientific interest due to its possible applications in the field of industrial biocatalysis [7]. Recently, Zare and his co-workers have developed a new method for creating hybrid organic-inorganic nanomaterial consisting of copper ions and various enzymes. The coordination between nitrogen atoms of the amide groups in enzymes and copper ions leads to a flower-like hybrid nanomaterial.

These protein-inorganic nanostructures result in an enhanced activity and stability of enzymes due to their large surface-to-volume ration and the cooperative interaction of the entrapped enzyme molecules [8].

In the present study, we have reported the preparation of enzyme-inorganic hybrid nanoflowers using copper (II) ions as the inorganic component and lipase B from *Candida anrarctica* as the organic component. Lipases are hydrolases that are promising enzymes for industrial applications [9]. In addition to their natural function of hydrolyzing ester bonds, these enzymes can catalyze esterification, transesterification and interesterification reactions in nonaqueous media [10]. The biocatalytic performance of lipase-nanoflowers for the hydrolysis of esters, as well as for the synthesis of lipophilic derivatives of natural phenolic antioxidants, has been determined in various third generation ionic solvents such as ionic liquids based on various hydroxyl ammonium cations and formic acid anion, as well as in choline chloride and ethyl ammonium chloride based deep eutectic solvents. Moreover, the stability and the reusability of lipase-nanoflowers in these environmentally friendly solvents has been investigated.

2. MATERIALS AND METHODS

Candida antarctica lipase B (CaLB) was obtained from Novozymes A/S (Denmark) and was used without further purification. Ethyl ferulate, 4-nitrophenyl butyrate, copper (II) sulfate pentahydrate and 1-octanol were purchased from Sigma. Choline chloride (ChCl), ethylammonium chloride (EAC), urea (U), glycerol (Gly), and ethylene glycol (EG) were of analytical grade and were obtained from Sigma-Aldrich, Merck or Applichem. The components of ILs (amines: 2-(methylamino) ethanol, 2-(dimethylamino)-ethanol, diethanolamine, ethanolamine and acids: formic acid, hexanoic acid, cyclopentanecarboxylic acid) were of the highest purity available (>99%) and were used without further purification.

2.1 DES and ILs synthesis

All ILs were prepared by neutralization of a carboxylic acid (formic acid, hexanoic acid and cyclopentanecarboxylic acid) with different amines (2-(methylamino)-ethanol, 2-(dimethylamino)-ethanol, diethanolamine and ethanolamine) as described elsewhere [11]. The reaction yields of all ILs synthesized were more than 97 % determined by ^{1}H-NMR and ^{13}C-NMR. DES were synthesized according to our previous study [12].

2.2 Preparation of CaLB-nanoflowers

CaLB nanoflowers were prepared according to previous study [8]. In brief, 1.4 mL of aqueous solution of $CuSO_4$ (120 mM) was added to 200 mL of phosphate buffer saline (PBS) (pH 7.4) containing 0.1 mg/mL CaLB. The mixture was incubated for three days at 25 ^{o}C. The nanoflower precipitates were collected after centrifugation, washed three times with water and dried under vacuum at room temperature. The concentration of protein in the supernatant after the immobilization was calculated using the Bradford assay and the immobilization yield of the protein

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was nearly 90 %. The size and the morphology of CaLB-nanoflowers were observed by a JSM 6510 LV (JOEL, Tokyo, Japan) electron microscope with an acceleration voltage of 20 kV.

2.3 CaLB-nanoflowers catalyzed synthesis of esters

In a typical transesterification reaction ethyl ferulate (20 mM), 1-octanol (120 mM) and 120 U mL^{-1} of CaLB-nanoflowers were added in various ILs or DES, previously dehydrated with 4 Å molecular sieves. In all cases, reaction mixtures were incubated at 700 rpm at 60 ^{o}C. 1 Unit of CalB corresponds to the amount of the enzyme that causes an increase in absorbance at 405 nm of 0.01 per minute at pH 7.5 at 25 °C in a reaction mixture containing 50 mM p-nitrophenyl butyrate. All experiments were performed in duplicate. Control experiments without enzyme were also carried out. The reaction was terminated by filtering off the biocatalyst, and the reaction mixture was diluted with methanol. The substrates and products of the biocatalytic reactions were quantified by HPLC analysis using a μBondapack C18 column, particle size 10 μm, length 300 mm, diameter 3.9 mm and a diode array UV detector. Gradient elution from 40% to 100% acetonitrile in water (containing 0.1% acetic acid) was employed for 30 min. The elution was performed at 35 ^{o}C at a flow rate of 1 mL/min. Total conversion yield was determined by the decrease in the amount of ethyl ferulate and expressed as the mean of three independent experiments.

2.4 CaLB –nanoflowers catalyzed hydrolysis of esters

CaLB-nanoflowers hydrolysis in various DES (containing 10 % v/v of 0.1 M Tris–HCl buffer pH 7.5) was started by adding 4-nitrophenyl butyrate (50mM, pNPB) in the reaction mixture containing 44 U mL^{-1} of the immobilized enzyme. 4-nitrophenol release was monitored at 405 nm at 2 minutes intervals for up to 20 minutes.

2.5. Stability studies of CalB-nanoflowers

Stability studies of CalB-nanoflowers in various DES were performed by incubating an amount of enzyme for different time intervals at 40 ^{o}C. Remaining lipase activity was determined by the enzymatic hydrolysis of pNPB as described above. The half-life times (t ½) were calculated from the one-step deactivation kinetics [13].

2.6. Reusability of CalB-nanoflowers

The reuse of the CalB-nanoflowers was studied by the determination of the residual enzyme activity in seven reaction cycles of ethyl ferulate transesterification with 1-octanol as described above. Each reaction was carried out for 24h at 60 ^{o}C. After each run, the immobilized enzyme was removed from the reaction mixture, washed thoroughly with ethyl acetate and then fresh substrate solution was added for the next reaction cycle.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization of CalB-nanoflowers

The incubation of $CuSO_4$ with a phosphate buffer saline containing CalB at room temperature for three days led to the creation of uniform flower-like spheres with an average of 20 μm diameter as depicted in a low resolution SEM image (Figure 1a). The high resolution SEM image showed that the morphology of the spheres was similar to the shape of a dahlia flower, assembled from hundreds of nanoplates (Figure 1b). It must be noted that, in the absence of the protein, no formation of nanoflowers was observed.

It has been proposed that nanoflower assembly follows a progressive process that begins with the formation of primary copper phosphate crystals. At this stage, aggregates are formed between protein molecules and Cu^{+2} mainly through coordination of amide groups in the protein backbone.

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These aggregates provide a location for nucleation of the primary crystals. The flower-like nanocrystals are gradually created from these nucleation sites, induced by the protein molecules which also serve as a "glue" to bind the petals together [8].

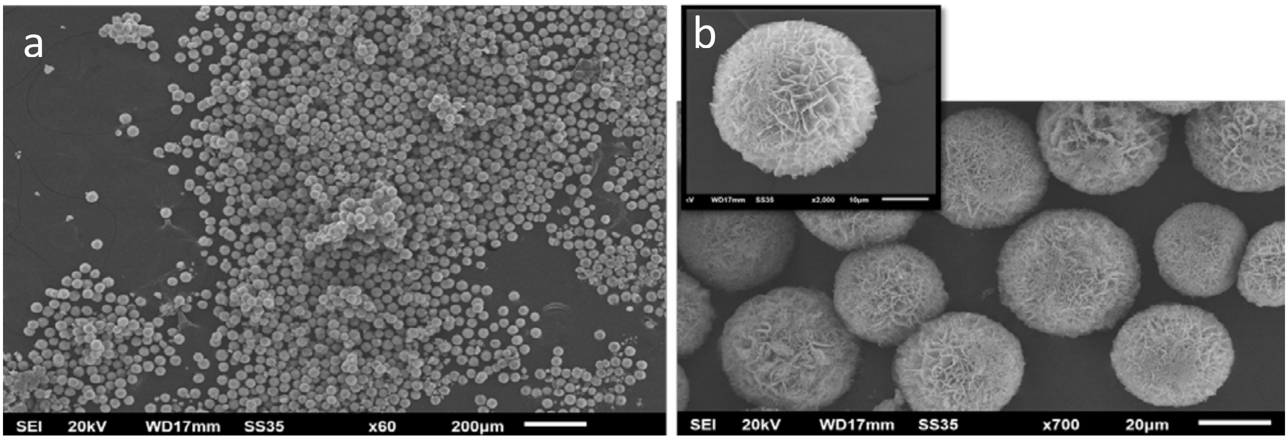


Figure 1. Scanning electron microscopy (SEM) images of CalB – copper phosphate nanoflowers at a) low and b) high resolution

3.2 Biocatalytic activity of CalB –nanoflowers in ionic solvents

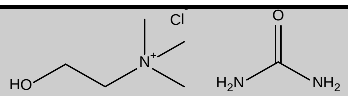
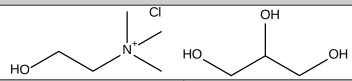
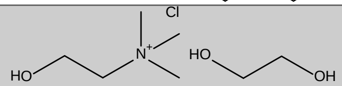
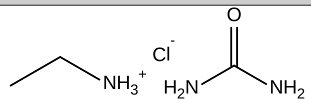
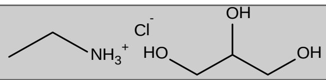
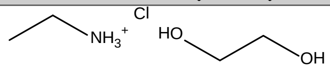
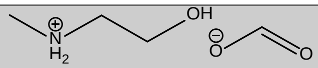
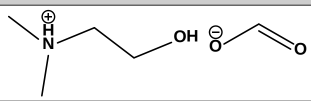
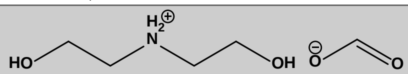
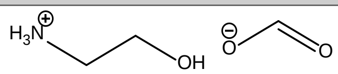
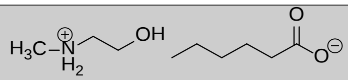
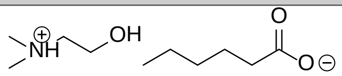
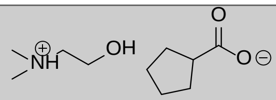
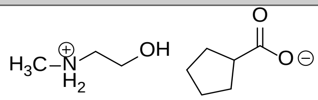
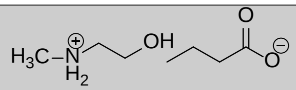
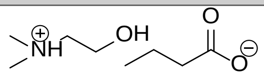
In the present study, the effect of six DES (ChCl:U, ChCl:Gly, ChCl:EG, EAC:U, EAC:Gly, EAC:EG) and ten hydroxyl ammonium third generation ILs (HMEAF, HDMEAF, BHEAF, HEAF, HMEAH, HDMEAH, HDMEAC, HMEAC, HMEAB, HDMEAB) on the activity of CaLB-nanoflowers has been investigated. It must be noted that, the use of DES as media for lipase catalyzed reactions has been reported before [14, 15]. However, the application of CaLB-nanoflowers in such solvents has been reported for the first time. The enzymatic transesterification of ethyl ferulate with 1-octanol at 60^{o}C was chosen as a model reaction. As it can be seen in Table 1, CaLB-nanoflowers could catalyze the transesterification of ethyl ferulate with 1- octanol, while this ability is greatly influenced by the nature of the ionic solvent used. In the case of DES, the use of EAC-based DES as reaction media, led to higher conversion yields compared to ChCl-based DES indicating that the nature of the salt used affects the activity of the enzyme.

The increased catalytic activity of CalB-nanoflowers observed in EAC-based DES could be attributed to the lower viscosity of these solvents compared to ChCl-based DES, that could decrease the mass transfer limitations of the substrates to the active site of the enzyme [16]. It must be noted that when Gly was used as HBD, a glyceryl ester formation was observed as a result of a transesterification reaction of Gly with the substrate, which was more obvious in the case of ChCl-based DES, as indicated in Table 1. When hydroxyl ammonium ILs were used as reaction media, low reaction yields were observed in all cases studied. This behavior could probably be attributed to the enzyme deactivation resulting from the high ability of these ILs to remove tightly bound water from the protein molecule, as previously reported for hydrophilic imidazolium ILs [17]. Moreover, it has been suggested that carboxylic anions of such ILs can form strong hydrogen bonds with the polypeptide backbone, which could result to the dissociation of the hydrogen bonds that maintain the structural integrity of the protein causing its whole or partial unfolding [18].

The use of DES as solvents for hydrolytic reactions catalysed by CaLB-nanoflowers has also been investigated using p-NPB as a substrate. As seen in Table 2, in some cases studied, the hydrolytic activity of CaLB-nanoflowers was increased, when DES were used as reaction media, compared to that observed in buffer. In particular, the reaction rates in EG-based DES were up to 2-fold higher compared to that in buffer, indicating the beneficial effect of these DES on the hydrolytic activity of immobilized enzyme.

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Table 1. Conversion yields for the enzymatic transesterification of ethyl ferulate (20 mM) with 1-octanol (120 mM) catalyzed by CaLB-nanoflowers (120 U mL^{-1}) in various reaction media at 60 ^oC after 72 h of incubation.

Reaction Media	Chemical Structure	Conversion Yield (%)
ChCl:U Choline Chloride urea		24.6 ± 2.4
ChCl:Gly Choline Chloride glycerol		13.0 (1.4)* ± 1.3
ChCl:EG Choline Chloride ethylene glycol		4.0 ± 0.9
EAC:U Ethylammonium chloride urea		42.5 ± 3.1
EAC:Gly Ethylammonium chloride glycerol		14.0 (<1)* ± 2.2
EAC:EG Ethylammonium chloride ethylene glycol		61.4 ± 3.8
HMEAF 2-hydroxy-N-methylethanaminium formate		0.8 ± 0.3
HDMEAF 2-hydroxy-N,N-dimethylethanaminium formate		4.7 ± 1.2
BHEAF Bis(2-hydroxyethyl)ammonium formate		0.7 ± 0.2
HEAF 2-hydroxyethyl ammonium formate		7.1 ± 1.1
HMEAH 2-hydroxy-N-methylethanaminium hexanoate		12.4 ± 2.7
HDMEAH 2-hydroxy-N,N-dimethylethanaminium hexanoate		6.4 ± 2.1
HDMEAC 2-hydroxy-N,N-dimethylethanaminium cyclopentanecarboxylate		6.5 ± 1.7
HMEAC 2-hydroxy-N-methylethanaminium cyclopentanecarboxylate		8.1 ± 1.3
HMEAB 2-hydroxy-N-methylethanaminium butyrate		15.8 ± 2.7
HDMEAB 2-hydroxy-N,N-dimethylethanaminium butyrate		15.8 ± 3.6

* Number in parentheses is the percentage conversion of the side reaction with the glycerol component of the deep eutectic solvent. No side reaction was detected in the other reactions.

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Table 2. Reaction rates (mM h^{-1}) of p-NPB hydrolysis catalyzed by CaLB-nanoflowers (44 U mL^{-1}) in 0.1 M phosphate buffer pH 7.5 and various deep eutectic solvents (90 % v/v) at 40^{o}C.

Deep eutectic Solvents	Reaction rate (mM h^{-1})
Buffer	7.8
ChCl:U	4.0
ChCl:Gly	5.1
ChCl:EG	15.8
EAC:U	8.4
EACl:Gly	4.9
EAC:EG	11.2

3.3. Stability of CalB –nanoflowers in DES

In order to further investigate the effect of DES on the biocatalytic behaviour of CaLB-nanoflowers, the stability of the immobilized lipase was studied in these media. After incubation of CaLB-nanoflowers in buffer and different DES at 40^{o}C, the remaining activity of CaLB-nanoflowers was determined using *p*-NPB as a substrate. Based on half-life times (Table 3), CaLB-nanoflowers were found to be more stable in most DES studied than in buffer.

Table 3. Estimation of half-life values ($t_{½}$) in hours of CaLB-nanoflowers in buffer and various DES.

Deep eutectic solvents	$t_{1/2}$ (h)
Buffer	1.1
ChCl:U	45.0
ChCl:Gly	56.8
ChCl:EG	3.1
EAC:U	1.0
EAC:Gly	3.5
EAC:EG	0.4

It must be noted that the half-life time of CaLB-nanoflowers increased up to 51 and 41-fold in ChCl:Gly and ChCl:U respectively, compared to that observed in buffer. Interestingly, the stability of the enzyme increased by the following order EG < U < Gly in both ChCl and EAC- based DES used. The high stabilizing effect of Gly as HBD for CaLB was also observed in a previous study [19]. These results clearly demonstrate that DES are not destructive to protein structure which maintain its catalytic activity after a longer term comparer to buffer.

3.4. Reuse of CalB –nanoflowers in DES

The efficient recyclability and reuse of DES was shown in our previous study [12]. In the present study we have investigated the reuse of the CaLB-nanoflowers in DES. For this purpose, the transesterification of ethyl ferulate with 1-octanol catalysed by CaLB-nanoflowers in EAC-EG has been used as a model reaction, in order to investigate the reusability of the immobilized enzyme. As it can be seen in Figure 1, when seven reaction cycles (168 h of total operation) were completed, the residual activity of the immobilized enzyme was 50%. Consequently, CaLB-nanoflowers could be successfully reused up to seven times in EAC-EG based-DES, indicating that these solvents could be considered as promising environmentally friendly media for the development of biocatalytic processes of industrial interest.

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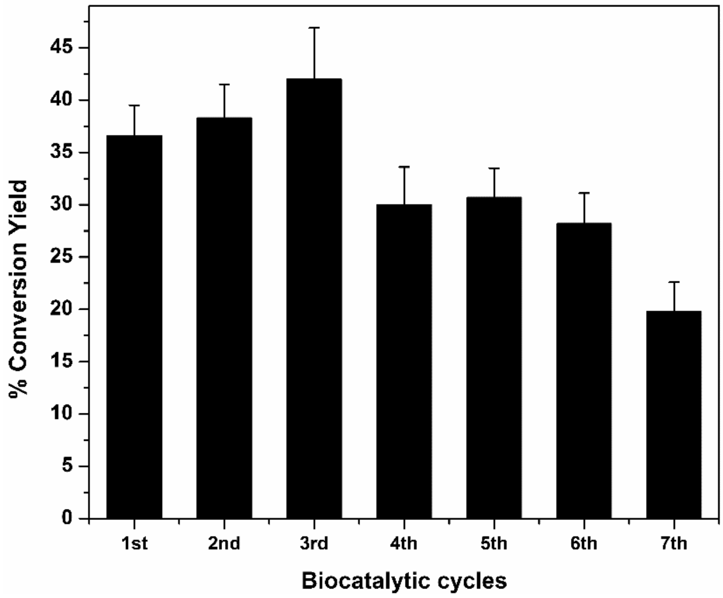


Figure 1. CaLB-nanoflowers activity after seven cycles of use for the enzymatic transesterification of ethyl ferulate (20 mM) with 1-octanol (120 mM) in EAC:EG at 60 ^oC after 24 h of incubation.

4. CONCLUSIONS

In the present study, we have shown that enzyme-inorganic hybrid nanoflowers are able to catalyse esterification and hydrolytic reactions in biodegradable, non-toxic and inexpensive third generation ILs and DES. The catalytic activity of lipase-nanoflowers strongly depends on the nature of the solvent used. DES have been proved to be better solvents than ILs for esterification or hydrolytic reactions catalysed by lipase-nanoflowers. The use of DES as reaction media significantly enhances the thermal stability of the immobilized enzyme compared to that observed in buffer. Moreover, lipase-nanoflowers could be efficiently reused up to seven times in DES, indicating the potential application of these novel solvents as media for the development of environmentally friendly biocatalytic processes with industrial interest.

References

[1] Sheldon, R. A., 2011. Characteristic Features and Biotechnological Applications of Cross-Linked Enzyme Aggregates (CLEAs). *Applied Microbiology and Biotechnology*, **92**, 467–77.

[2] Wenda, S., Illner, S., Mell, A., Kragl, U., 2011. Industrial Biotechnology—the Future of Green Chemistry? *Green Chemistry*, **13**, 3007.

[3] Lozano, P., 2010. Enzymes in Neoteric Solvents: From One-Phase to Multiphase Systems. *Green Chemistry*, **12**, 555.

[4] Domínguez de María, P., Maugeri, Z., 2011. Ionic Liquids in Biotransformations: From Proof-of-Cocept to Emerging Deep-Eutectic-Solvents. *Current Opinion in Chemical Biology*, **15,** 220–25.

[5] Ventura, S. P. M., Santos, L. D. F., Saraiva, J. A. Coutinho, J. A. P., 2012. Ionic Liquids Microemulsions: The Key to *Candida antarctica* Lipase B Superactivity. *Green Chemistry*, **14,** 1620.

[6] Sheldon, R. A., 2007. Enzyme Immobilization : The Quest for Optimum Performance. *Advanced Synthesis and Catalysis*, **349**, 1289-1307.

[7] Pavlidis, I., V, Patila, M., Bornscheuer, U. T., Gournis, D., Stamatis, H., 2014. Graphene-Based Nanobiocatalytic Systems: Recent Advances and Future Prospects. *Trends in Biotechnology*, **32**, 312–20.

[8] Ge, J., Lei, J., Zare, R. N., 2012. Protein–inorganic Hybrid Nanoflowers. *Nature Nanotechnology*, **7**, 428–32.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[9] Singh, A. K., Mukhopadhyay, M., 2012. Overview of Fungal Lipase: A Review. *Applied Biochemistry and Biotechnology*, **166,** 486–520.

[10] Papadopoulou, A. A., Katsoura, M. H., Chatzikonstantinou, A., Kyriakou, E., Polydera, A. C., Tzakos, A. G., Stamatis, H., 2013. Enzymatic Hybridization of α-Lipoic Acid with Bioactive Compounds in Ionic Solvents. *Bioresource Technology*, **136**, 41–48.

[11] Papadopoulou, A. A., Tzani, A., Alivertis, D., Katsoura, M. H., Polydera, A. C., Detsi, A., Stamatis, H., 2016. Hydroxyl Ammonium Ionic Liquids as Media for Biocatalytic Oxidations. *Green Chemistry*, **18**, 1147-1158.

[12] Papadopoulou, A.A, Efstathiadou, E., Patila, M., Polydera, A. C., Stamatis, H., 2016. Deep Eutectic Solvents as Media for Peroxidation Reactions Catalyzed by Heme-Dependent Biocatalysts. *Industrial and Engineering Chemistry Research*, Special Issue: International Conference on Chemical and Biochemical Engineering 2015.

[13] Henley, J. P., Sadana, A., 1985. Categorization of Enzyme Deactivations Using a Series-Type Mechanism. *Enzyme and Microbial Technology,* **7,** 50–60.

[14] Gorke, J. T., Srienc, F., Kazlauskas, R. J.,. 2008. Hydrolase-Catalyzed Biotransformations in Deep Eutectic Solvents. *Chemical Communications*, **10**, 1235–1237.

[15] Huang, Z. L., Wu, B. P., Wen, Q., Yang, T. X., Yang, Z., 2014. Deep Eutectic Solvents Can Be Viable Enzyme Activators and Stabilizers. *Journal of Chemical Technology & Biotechnology,* **89** 1975–1981.

[16] Durand, E., Lecomte, J., Baréa, B., Piombo, G. Dubreucq, E., Villeneuve, P., 2012. Evaluation of Deep Eutectic Solvents as New Media for Candida Antarctica B Lipase Catalyzed Reactions. *Process Biochemistry,* **47**, 2081–2089.

[17] de los Ríos, A. P., Hernández-Fernández, F. J., Tomás-Alonso, F., Gómez, D., Víllora, G., 2008. Synthesis of Flavour Esters Using Free Candida Antarctica Lipase B in Ionic Liquids. *Flavour and Fragrance Journal* **23**, 319–322.

[18] Rantwijk, F. V., Secundo, F., Sheldon, R. A., 2006. Structure and Activity of *Candida antarctica* Lipase B in Ionic Liquids. *Green Chemistry,* **8**, 282-286.

[19] Kleiner, B., Schörken, U., 2015. Native Lipase Dissolved in Hydrophilic Green Solvents: A Versatile 2-Phase Reaction System for High Yield Ester Synthesis. *European Journal of Lipid Science and Technology,* **117**, 167–177.

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Environmental Law and Policy

PROTECTION
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OF THE
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XIII

Approaches to determine hazard properties for EU waste classification

P. Maraboutis*, E. Nikolaou, N. Poulimenou

Eco-efficiency Consulting and Engineering Ltd., Athens, Haidari, 12462, Greece.
*Corresponding author: Email: p.maraboutis@ecoefficiency.gr

Abstract

The assessment and the evaluation on the classification of waste are applied to each distinctive waste stream, which is generated by a waste producer. The classification of a waste is under the principles of the Waste Framework Directive 2008/98/EC (WFD), which was directly affected by the Regulation (EC) 1272/2008 on the Classification Labelling and Packaging of substances and mixtures (CLP), by means of hazard classes and categories. In particular, the properties that render waste hazardous have been updated by Commission Regulation 1357/2014 amending Annex III to Directive 2008/98/EC (Waste Framework Directive). Additionally, Commission Decision 2000/532/EC (European List of Waste) has been revised by EU Decision 2014/955/EU. This paper wishes to shed light on the procedure and the approaches to determine EU waste classification.

Keywords: waste classification; hazardous properties; EU legislation; LoW; Directive 2008/98/EC

1. INTRODUCTION

The assessment and the evaluation on the classification of waste are applied to each distinctive waste stream, which is generated by a waste producer. The evaluator should examine every waste separately when more than one waste is produced. The classification of a waste is under the principles of the Waste Framework Directive 2008/98/EC (WFD) [1] and it must not be confused with the criteria for acceptance of waste as set out by the Landfill Directive. The WFD is directly affected by the Regulation (EC) 1272/2008 on the Classification Labelling and Packaging of substances and mixtures (CLP), by means of hazard classes and categories. Furthermore, it has to be assessed whether certain specified waste streams are excluded from the scope of the WFD.

Nearly all household, commercial and industrial waste needs to be classified [2]. Every waste stream whether it is included or not from the scope of WFD is to be classified according to the European List of Waste (Decision 2000/532/EC, as amended by the EU Decision (EU) 2014/955 - LoW) [3]. Furthermore, the criteria and the limit values for the proper classification have been recently revised and now they are under the scope of The Regulation (EU) No. 1357/2014 on the replacement of Annex III to Directive 2008/98/EC [4].

The hazard assessment of a waste is based on 15 hazardous properties (HP1 to HP15) which must be separately examined. (The hazardous properties H1 to H15, as defined in Annex III to Directive (EC) 2008/98, were renamed as HP1 to HP15). However the definition of the 15 hazard properties of waste has not been completed, since the attribution of the hazardous property HP 14 is made on the basis of the criteria laid down in Annex VI to Council Directive 67/548/EEC. The assessment of HP 14 has not been changed to allow time for Directorate General of the Environment of European Commission to complete a study that is examining the impacts of four different calculation methods. The legislation limited the first two levels of chronic ecotoxicity, but including extended M-factors [5].

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The assessment starts with the investigation and identification of hazardous ingredients, which may be contained in the waste and compare their content based on the limit values defined in Regulation 1357/2014/EU. Chemical analyses (particularly for inorganic substances) do not always identify the specific components but may only identify the individual anions and cations. In such cases, the waste holder/ evaluator may need to determine what precise substances are likely to be present either by further analysis or by applying knowledge of the process / activity that produced the waste. If there is any doubt, the worst case substance should be considered to be present [2]. Another way is to derive mineralogical forms of the elements from leachate composition at different pH and geochemical modeling [6]. If necessary, the risk assessment may require of specific tests per hazardous property for the waste. If testing is considered for the determination of a hazard property, the performance should be in accordance with the Regulation (EC) No 440/ 2008 or other internationally recognized test methods and guidelines, taking into account Article 7 of Regulation (EC) No 1272/2008, that tests on animals shall be undertaken only where no other alternatives exist. The aforementioned legal analysis as to waste identification and classification is a tool for sustainable eco management, which achieves long living restoration systems. According to the adopted legislation a waste producer shall not mixed hazardous waste, either with other categories of hazardous waste or with other waste, substances or materials. Therefore, in order to promote the techniques of proper restoration, every waste stream should be evaluated in order to make certain that the mixing of wastes as backfilling or construction material activities harm neither the environment nor the human.

2. LEGISLATIVE FRAMEWORK

2.1 Waste Framework Directive 2008/98/EC

The Waste Framework Directive (WFD) sets the key concepts and the basic definition related to waste management. The directive establishes what waste is and defines the principles of waste management.

According to article 3 of the WFD a hazardous waste defined as a waste which displays one or more of the hazardous properties listed in Annex III. The application of this Annex is completed by the characterization of a waste as hazardous or non-hazardous by the appropriate six-digit code from the List of Wastes (LoW); article 7 of the WFD establishes the basic principles for the LoW.

Both the Annex III of the WFD and Decision 2000/532/EC (List of Wastes) have been recently adapted to scientific progress and have been replaced by the above regulations:

- Commission Regulation 1357/2014 replaces the Annex III to Directive 2008/98/EC. The new Hazardous Properties (HP) are to be applied as of 1 June 2015,
- The EU Decision 2014/955/EU amends Decision 2000/532/EC on the list of waste pursuant

2.2 European List of Waste (LoW)

Commission Decision 2000/532/EC establishes the European List of Waste (LoW). The last amendment to the LoW, has been conducted by the EU Decision 2014/955/EU, in order to adapt the scientific progress that have been set by chemicals legislation. Legally, the LoW should have been applied since 1 June 2015. The procedure of the evaluation whether the waste is hazardous or not is a decision-making process that typically begins with the European Waste Catalogue, in which both the hazardous and the non-hazardous wastes are included [7].

The different types of waste in the list are fully defined by the six-digit code. The LoW contains 20 chapters (two digit codes), further divided into sub-chapters (four digit codes) and entries (six digit codes). The six-digit codes that are marked by an asterisk (*) shall be consider as hazardous. On the other hand all the other entries are considered as non- hazardous.

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The methodology for the selection of the appropriate code for every waste stream is based on the identification of the source generating the waste, by choosing the first 2 digits from the Chapters 01 to 12 or 17 to 20. If no appropriate waste code can be found in Chapters 01 to 12 or 17 to 20, the Chapters 13, 14 and 15 must be examined to identify the waste. As last choice the waste must be identified according to Chapter 16. If the waste is not in Chapter 16 either, the 99 code (wastes not otherwise specified) must be used in the section of the list corresponding to the activity identified in step one.

The identification of the most appropriate entry is an important step in the classification of waste and requires a sound judgement by the evaluator of a waste, based on his knowledge of the origin and process generating the waste, as well as its potential composition.

2.3 Mining waste Directive

The subject of the Directive 2006/21/EC [8] is to provide measure, procedures and guidance to prevent or reduce as far as possible any adverse effects on the environment, in particular water, air, soil, fauna and flora and landscape, and any resultant risks to human health, brought about as a result of the management of waste from the extractive industries.

Although, according to Article 2 of the WFD, the waste resulting from prospecting, extraction, treatment and storage of mineral resources and the working of quarries are not covered from the WFD, the waste evaluator should classify the waste from the extractive industries according to criteria of LoW.

2.4 The Landfill Directive

The Directive 1999/31/EC [9] defines the different categories of waste (municipal waste, hazardous waste, non-hazardous waste and inert waste) and applies to all landfills, defined as waste disposal sites for the deposit of waste onto or into land. Landfills are divided into three classes:

- landfills for hazardous waste;
- landfills for non-hazardous waste;
- landfills for inert waste.

The criteria and the procedures for the acceptance of a waste under the Landfill Directive set out in Annex II. Although, the classification of waste as hazardous according to LoW and Annex III to the WFD is important also for the purposes of the landfill, since hazardous waste should be disposed in landfills for hazardous waste, and non-hazardous waste shall be disposed in landfills for non-hazardous waste or inert waste.

3. PROCEDURES FOR THE CLASSIFICATION OF WASTE

The assessment and classification of waste is applied to each distinct waste stream generated by a producer. All waste streams not excluded by the WFD are to be classified according to WFD and the LoW, as it is given in the Figure 1. As a second step, the waste evaluator should identify the most appropriate entry for any given waste stream in the LoW. The question that arises is in which entry the waste stream shall be assigned (a) absolute hazardous entry, (b) absolute non-hazardous entry or (c) Mirror entry

- **Absolute hazardous entry**: The waste stream is marked with an asterisk and must not be allocated in a non-hazardous entry. It will still be necessary to proceed in the evaluation of the 15 hazardous properties of the Annex to Regulation 1357/2014/EU, in order to fulfill the provisions laid down in Article 19 of the WFD on correct labeling of hazardous waste (e.g. for filling a consignment note for waste movements). The Table 1 provides an overview of the 15 hazardous properties.

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- **Absolute non-hazardous entry**: In case a waste stream is non-hazardous shall be classified as non-hazardous without any further assessment
- **Mirror entry:** Mirror entries are a group of at least two alternative entries. It is necessary to proceed in the evaluation of the 15 hazardous properties of the Annex to Regulation 1357/2014/EU, in order to determine, in which entry, the mirror hazardous or the mirror non-hazardous shall be allocated. If the waste displays one or more of the 15 hazardous properties, the corresponding hazardous entry has to be assigned.

Table 1. Hazardous properties of the Annex to Regulation 1357/2014/EU

HP1	"**Explosive**": It refers to the waste which is capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic waste, explosive organic peroxide waste and explosive self-reactive waste is included.
HP2	"**Oxidising**": It refers to the waste which may, generally by providing oxygen, cause or contribute to the combustion of other materials.
HP3	"**Flammable**": It refers to the waste witch applies to at least one of the following : — flammable liquid waste: liquid waste having a flash point below 60 °C or waste gas oil, diesel and light heating oils having a flash point > 55 °C and ≤75 °C; — flammable pyrophoric liquid and solid waste: solid or liquid waste which, even in small quantities, is liable to ignite within five minutes after coming into contact with air; — flammable solid waste: solid waste which is readily combustible or may cause or contribute to fire through friction; — flammable gaseous waste: gaseous waste which is flammable in air at 20 °C and a standard pressure of 101.3 kPa; — water reactive waste: waste which, in contact with water, emits flammable gases in dangerous quantities; — other flammable waste: flammable aerosols, flammable self-heating waste, flammable organic peroxides and flammable self-reactive waste.
HP4	"**Irritant —skin irritation and eye damage**": Waste which on application can cause skin irritation or damage to the eye.
HP5	"**Specific Target Organ Toxicity (STOT)/Aspiration Toxicity**": waste which can cause specific target organ toxicity either from a single or repeated exposure, or which cause acute toxic effects following aspiration.
HP6	"**Acute Toxicity**": waste which can cause acute toxic effects following oral or dermal administration, or inhalation exposure.
HP7	"**Carcinogenic**": waste which induces cancer or increases its incidence.
HP8	"**Corrosive**": waste which on application can cause skin corrosion.
HP9	"**Infectious**": waste containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.
HP10	"**Toxic for reproduction**": waste which has adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring.
HP11	"**Mutagenic**": waste which may cause a mutation, that is a permanent change in the amount or structure of the genetic material in a cell.
HP12	"**Release of an acute toxic gas**": waste which releases acute toxic gases (Acute Tox. 1, 2 or 3) in contact with water or an acid.
HP13	"**Sensitising**": waste which contains one or more substances known to cause sensitising effects to the skin or the respiratory organs.
HP14	"**Ecotoxic**": waste which presents or may present immediate or delayed risks for one or more sectors of the environment.
HP15	"**Waste capable of exhibiting a hazardous property listed above not directly displayed by the original waste**".

According to this approach the determination if a waste is hazardous or non-hazardous is based on the 15 hazardous properties (HP1 to HP15) of the Annex to Regulation 1357/2014/EU, which must be separately examined. The assessment starts with the investigation and the identification of the hazardous ingredients, which may be contained in the waste and compare their content based on the limit values defined in Regulation 1357/2014/EU. In order to evaluate the hazardous ingredients in

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the waste and subsequently to be able to perform the assessment, it is necessary to obtain sufficient information about the presence and content of hazardous substances in the waste, in order to be able to determine if the waste might display any of the hazardous properties HP1 to HP15. Regarding the calculation method, it should be noted that hazardous substance content values in waste as they have been determined, e.g. by sampling and chemical analysis of the waste under consideration, have to be compared against the concentration limits listed in Regulation 1357/2014/EU.

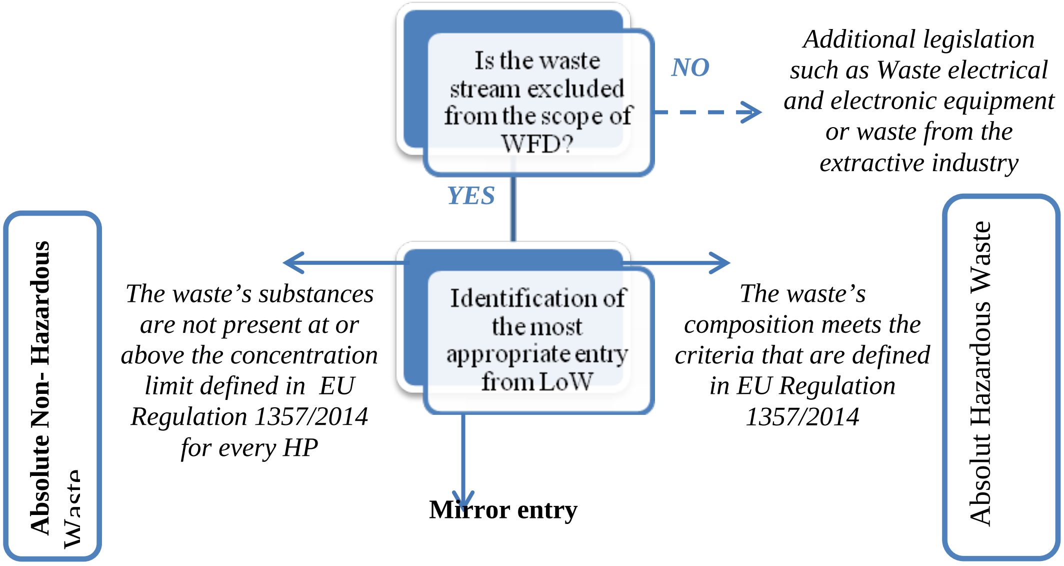


Figure 1. Flow chart for the evaluation of a waste stream

4. IMPLEMENTATION OF THE WASTE CHARACTERIZATION ON REVEGETATION AND RESTORATION ISSUES

When an operation comes to an end, the site needs to be prepared for subsequent use, although, it is impossible to restore a site on its original condition. Usually, the aftercare phase is the responsibility of the operator; however the operator, the authorities and the stakeholders involved should agree on the successive use [10]. Land restoration by means of the mining waste extracted during operations allows for better land rehabilitation results. Usually, the materials used for the restoration of a land, by means of backfilling, are tailings mixed with a binder, usually cement, and then pumped underground to fill voids and help support the restoration procedures [11].

Taking into consideration the Article 5 of the Mining Waste Directive "*…placing extractive waste back into the excavation void after extraction of the mineral, as far as is technically and economically feasible and environmentally sound in accordance with existing environmental standards at Community level…*" the land restoration should be based firstly on the security of the stability of the area and secondly the operator should take appropriate measures to prevent the pollution of the environment and the adverse effects on human health.

Although, the Mining Waste Directive is excluded from the scope of the WFD, according to the WFD and the Article 18 it is forbidden to mix hazardous wastes either with other categories of hazardous waste or with other waste, substances or materials. For this reason the procedure of restoration by means of backfilling, shall be accompanied with the waste classification according to the WFD and the LoW and it must not be confused with the criteria for acceptance of waste as set out by the Landfill Directive. Furthermore, the tailings and the waste used for the restoration

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procedures should be evaluated according to the HP1 – HP15 in order to recognize in which group entry the waste shall be assigned and is it should be used in the restoration.

As far as the revegetation procedure is concerned, the operator should fulfill the fundamental criteria for closure processes, which are the physical, the chemical and the biological stability of the area. Specifically, when the environment is restored to a natural, balanced ecosystem typical of the area the natural rehabilitation can occur.

5. CONCLUSIONS

The EU waste law has raised the concern on the impact of the waste management for health and the environment. The revision of the legislation has been conducted, in order to reinforce and simplify the existing procedures of waste classification and takes into consideration the Regulation (EC) 1272/2008 on the Classification Labelling and Packaging of substances and mixtures. Nowadays, the recognition if a waste is hazardous or nonhazardous is a crucial decision in the entire chain of waste management and of life – cycle of an operation. The final step of the life cycle of an operation is the restoration and the after care of a facility. The proper classification of a waste stream, by means of backfilling, can promote the process of natural rehabilitation.

REFERENCES

[1] Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.
Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0098

[2] Scottish Environment Protection Agency (SEPA), Natural Resources Wales, Northern Ireland Environment Agency (NIEA), Environment Agency, 2015. *Guidance on the classification and assessment of waste.* 1st edition 2015

[3] Commission decision of 18 December 2014 amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv%3AOJ.L_.2014.370.01.0044.01.ENG

[4] Commission regulation (EU) No 1357/2014 of 18 December 2014 replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives
Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv%3AOJ.L_.2014.365. 01.0089. 01.ENG

[5] Hennebert, Humez, Conche, Bishop, Redischung, 2015. *Assessment of four calculation methods proposed by the EC for waste hazardous property HP 14 'Ecotoxic'.* Waste Management **48** pp 24-33

[6] Hennebert, Papin, Padox, Hasebrouck, 2013. *The evaluation of an analytical protocol for the determination of substances in waste for hazard classification*. Waste Management **33** pp 1577-1588

[7] Georgalas, Maraboutis, Nikolaoy, Xenidis, 2012. Methodology and strategy for evaluation of hazardous properties of waste: current guidelines, difficulties and possible solutions. *Proceedings of the International Conference on Management of Solid Waste - Hellenic Solid Waste Management Association, December 2012 National Technical University of Athens*

[8] Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC
Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32006L0021

[9] Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste
Available on: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31999L0031

[10] Europe Commission, 2009. *Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities*

[11] Tailings.info. *Backfill of Tailings to Underground Workings*. Available on: http://www.tailings.info /storage/backfill.htm

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Creating a compensation fund: towards a more effective solution to the environmental prevention and restoration?

K. Pouikli

Attorney at Law, PhD Candidate in Environmental Law at the Aristotle University Law School,
54124 Thessaloniki, Greece.
Email: kleoniki.pouikli@gmail.com

Abstract

The major problem concerning the prevention and restoration of environmental damage consists in the complicated and non linear nature of the environmental harmful effects as well as in their very difficult evaluation, since the environmental resources themselves have no commercial or monetary value. In this framework, the Directive 2004/35/EC on environmental liability (ELD) excludes any monetary preventive or remedying measure by providing for a triple mechanism of *in natura* measures. However, the efficient enforcement of these provisions has to overcome the hurdles of the establishment of the causal link and of the assessment of environmental damages. These obstacles are insuperable given the fact of the diffuse character of many damages, the multiple source environmental risks, the lack of mandatory financial security provision in the ELD, the possible insolvency of the responsible polluters. Hence, the perspective of setting up a compensation fund seems to be a more and more attractive regarding the more effective deal with environmental damages, despite the expressed criticism regarding the very famous american Superfund (CERCLA). Therefore, the aim of this paper is to explore the feasibility of designing such a fund as well as its particular characteristics in order to be consistent with the polluter pays principle.

Keywords: environmental damage; compensation fund; prevention; restoration; polluter pays principle

1. INTRODUCTION

The Directive 2004/35/EC on “environmental liability with regard to the prevention and remedying of the environmental damage” entered into force on 30 April 2004, with a transposition deadline set for April 2007. The Environmental Liability Directive (hereinafter referred to as “ELD”) has been completed transposed by all Member States since June 2010. This Directive aspired to establish an effective model of environmental liability based on the Polluter Pays Principle (hereinafter referred to as “PPP”) that would offer solutions to environmental problems, which are distinguished by the lack of spatial and temporal limits as well as by their dynamic, diffuse and no linear development. The ELD makes Member States responsible for ensuring that significant and measurable damage to water, land, and biodiversity (protected species and habitats) is either prevented by appropriate measures in case of imminent threats, or effectively remedied by restoring the previous condition, if the damage has already been done.

Moreover, the ELD outlines in Annex III the activities for which an operator may be held liable, a set of exemptions as well as certain obligatory and optional defences. The fundamental characteristic of this Directive is the break with the traditional civil law liability models and the establishment -after more than ten years of deliberations and several unsuccessful legal choices [1],

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of a *sui generis* both strict and fault based liability regime that deals straightforward with the pure environmental damage, reinforces the preventive action and emphasizes the need for *in natura* restoration by providing for a triple system of primary, compensatory and complementary remediation[2] .

The adoption of the ELD sparked off an important legal debate regarding the financial security and insurance issues related to the environmental damages. Given that the ELD implements the PPP, its main aim consists in making the liable operators bear the cost for restoration of the environmental damage they cause. However, the EU Parliament and the Council recognizing promptly the risk that environmental damages will not be restored in cases of operator's insolvency, activation of defences established by the ELD or of diffuse damage. According to this, Member States encourage the use by operators of appropriate financial security and the development of financial security instruments and markets in order to provide effective cover for financial obligations under this Directive. However, the ELD does not oblige operators to take up financial security through concrete predetermined solutions before environmental damage has occurred. Despite the fact that the European Parliament made a proposal to include such a provision, the Council deleted it during the legislative process. In lieu of mandatory financial security the ELD was confined only to a declaratory encouragement towards the development of financial security mechanisms [3].

That constitutes a major problem, given that the remediation of environmental damage can be extraordinarily costly. In particular, the occasion that reactivated the discussion regarding the deficits of the existing provisions as well as the potential setting up of a compensation fund for environmental damages was a red sludge catastrophe in Hungary in 2010 with tremendous consequences [4]. Similar EU cases that had already underlined this crucial issue were the Aznalcollar disaster (1999), the AZF Disaster in Toulouse (2001) and the Prestige oil tanker disaster (2002). In this framework, it is essential to explore the possibility of creating a compensation fund as an alternative financial compensation mechanism covering environmental liabilities.

2. THE INEFFICIENT FINANCIAL SECURITY MECHANISMS IN EU LANDSCAPE

The need for alternative financial assurances stems from the deficiencies of the general system of liability law and liability insurance. The latter has been demonstrated not to be fully satisfactory for ensuring the compensation of personal injury, property damages and remediation costs resulting from pollution and other adverse effects on the environment [5]. As "financial security" may be generally characterized a financial instrument put in a place by any operator prior to the occurrence of any environmental damage that provides a defined maximum amount of money readily available to third parties upon the occurrence of environmental damage during a specified, fixed period, regardless of the financial capacity of the operator at the time[6]. Through the lens of the ELD, the financial security can help to provide the funds for restoration in cases of unidentified, unavailable or insolvent operator [7]. In this respect, the term "financial security" refers to all instruments that provide financial security, including cash deposits, bonds, bank guarantees, other third party guarantees, mutual insurance arrangements, self-insurance, and insurance provided by a third party insurer [8].

The cornerstone of a financial security system based on the idea that these instruments ensure the availability of liquid asset whenever a triggering event occurs; however, the coverage limit is determined and the maximum coverage of a financial security instrument should have a rational relation with the maximum reasonably predictable damage. At this specific point can be identified the challenging function of the financial security mechanisms in the field of environmental liability,

since the environmental damages are characterized often by their dynamic, unpredictable and diffuse nature.

Accordingly, whilst the abovementioned security instruments have been successfully used in other areas, their application in the area of environmental damage has proved to be complicated and is still far from being mature, mainly driven due to late ELD implementation by Member States [9]. In addition to this, at the time of the ELD's adoption in 2004, the market for financial securities in the EU landscape was fragmented [10]. Reflecting the differences in national law and practice, it was organized at the national rather that European level and the experience with natural resource damage was very limited. Therefore the EU-wide environmental liability has demonstrated slow growth regarding the financial security market.

In this framework, EU has trouble gathering examples of ELD claims and there is a lack of data available for predicting potential environmental risks mainly due to legal ambiguities of the ELD. Particularly, there is lack of widespread definition of what constitutes "baseline condition" and vague definition for threshold of damage severity. Moreover, among the EU Member States is figured out a differentiated implementation of the defences and the scope of the activities considered for strict liability. In this vein, further adversities in the field of environmental damage arise by virtue of the limited financial security market: environmental insurers have specialized expertise and new products being slowly developed for new ELD risks due to the not easily calculable environmental harm. Lastly, financial security products are limited and very expensive and information on accidents and costs not yet widely available.

This EU immaturity and fragmentation with respect to the financial security is confirmed in October 2010, when the European Commission concluded that there was not sufficient justification at that time to introduce a harmonized system of mandatory financial security [11] due, among other things, to the lack of practical experience in the implementation of the ELD resulting from a three-year delay in its transposition in some Member States. Nevertheless, the ELD does not preclude Member States from issuing more stringent provisions [12]. In that context, some Member States have already enacted legislation to introduce mandatory financial security for ELD liabilities (Spain, Greece, Portugal, Bulgaria, Hungary, Czech Republic, Romania and Slovakia), but the effective implementation of these legislations stumbles over practical difficulties [13].

Namely, the perspective of a mandatory financial security raises very crucial issues concerning the included operators, the amount of premium, the terms and conditions of its activation, the coverage limit, and the potential exceptions. Even more important, however, is the question whether the particular financial security instruments should be imposed by the Member States or chosen by the operators. The second alternative seems to be more appropriate because otherwise the decision for one instrument will likely be arbitrary and create a "captured market" with possible uncompetitive pricing but without assuring the required coverage [14]. Moreover, another objection as far as the mandatory insurance is concerned refers to the function of such an instrument as a disincentive for the operator's optimal care for environmental risks [15].

Under these circumstances, only Spain and Hungary were among the Member States that adopted and set into force compulsory systems underlying the complicated nature of this issue. In Spain, indicatively, the Article 26 of the Spanish FSM Law allows for any or all of the following types of financial security: 1) an insurance policy from a Spanish-licensed insurer; 2) a financial guarantee secured by a Spanish-licensed financial institution; or 3) an ad hoc endowment reserve fund created by the Spanish FSM Law and supported by the public sector [16]. Further, the Spanish system requires coverage for amounts over €300000 (floor) up to €20 million (ceiling) per annum [17], while it limits the financial security requirement to activities posing an assessed "risk of pollution", that is narrower than the ELD term "environmental damage". Exception to the general rule of mandatory financial security is established for operators that operate an activity certified pursuant to either the EU EMAS regime or the International Organization for Standardization's ISO 14001 standard [18].

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In view of the above analysis, it is clear that the financial security and insurance provisions in the EU level has a fragmented and inefficient character, since they do not cover all environmental damage within the scope of the ELD. Furthermore, the –so far– proposed solutions on this issue remain piecemeal and national law-oriented.

3. THE FEASIBILITY OF A COMPENSATION FUND FOR ENVIRONMENTAL DAMAGES

The lack of an efficient, coherent and harmonized financial security system for environmental damages in EU level in combination with the increase of environmental risks as well as the aggravation of environmental disaster addresses the issue of establishing a compensation fund as an alternative viable answer to the complicated environmental cases. Additionally, the limitation of the insurance market as well as the very slow progress on the development of new products do not correspond to the increasing demand for financial assurances for environmental liabilities under the legal requirements in force[19].

In this vein, despite the strong criticism that has been levelled against the option of a compensation fund[20], such a choice may constitute a potential solution, given that under certain conditions both the existing liability regimes and the premature financial security mechanisms do not provide for adequate answers to the extremely complex structure of current environmental phenomena. The main drawback related to the establishment of such a fund consists in its contrast to the PPP, which constitutes the basement of the ELD. In the ideal world, according to the PPP the companies, which caused damages, should be liable for the entire amount and financial security covers only any excess amount they will be unable to fund. In practice, a balance between the costs and benefits of full protection against any potential inability to compensate damage must be found, and less than perfect financial security is likely to be the preferred policy option[21]. On these grounds, it must be ensured that a fund or scheme that spreads the risk and pre-financing of claims from a major accident will not relieve the liable operator from the financial consequences of its act and its legal liabilities. In order to comply with the polluter-pays principle, therefore, the proposed fund must not affect any incentives to operators to avoid damage from their activities and must not allow operators to profit from wrongdoing.

Being at this crossroads and due to the fact that the function of such a compensation fund may undermine the application of the PPP, it should be underlined that its activation should have a guarantee or complementary character and be strictly limited inasmuch as it is impossible for the liability rules and the financial security mechanisms in force to apply. In general, it is very crucial to determine tirelessly the criteria for the activation of such a potential compensation fund especially as far as the identification of the included environmental damages, the circle of potential polluters (and of the fund) and the amount of their contribution is concerned.

The European Commission realizing the extent of the problems raised by the lack of stable and effective answer to the environmental liability and financial security issues, decided to carry out a specific study focused on the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents[22]. The "trigger" for this initiative was a major industrial accident that took place at the MAL alumina factory near Kolontár, Hungary on 4 October 2010[23]. In the wake of this huge environmental disaster, the Hungarian government proposed the establishment of a European Union Industrial Disaster Risk-Sharing Facility to be funded by an annual contribution from targeted industries and companies[24]. The amount of the contribution would be indexed in accordance with the annual net corporate income of companies in the targeted industrial sector.

The idea was very challenging and has given rise to a considerable interest among Member States, public authorities, industry sector and experts from the Commission. Whilst the proposition

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highlighted urgently the need to account more efficiently for the environmental damage caused by disasters of such a magnitude, it has actually thrown up more questions than it solves. Although such propositions of creating a fund or risk sharing pools to cover liabilities are not new and have already been materialized in the international ambit, like the voluntary compensation scheme OPOL (Offshore Pollution Liability Association) which covers accidents from off-shore oil and gas operations in N. Atlanta, the ongoing progress with the EU is slow-paced. Moreover, this idea may not be so acceptable from the industrial sectors which could provide for their liabilities using other approaches and tools.

This is due to a whole series of reasons in connection with the outline of key design elements of potential fund. Namely, the main questions focuses on the key sectors as well as the types of damages to be covered, the nature of liabilities, the specific scheme of the fund and the way the fund is raised. In addition to this, burning issues regarding the concrete function of the fund concern its general or the sectoral character, its EU-wide or regional cover, its size and its threshold as well as how the key stakeholders will be engaged in such a scheme. Apart from all these, a cardinal problematic is related to management of the fund: who will make decision for the resources of the fund and who will exercise the monitoring procedure.

To sum up, it is undeniable that the proposition of introducing a compensation fund in order to deal more efficiently with the environmental liabilities constitutes an ambitious and controversial task. The legal ambiguities regarding the features and the function of such a scheme as well as the conflict with the PPP constrain admittedly this perspective. In the light of the foregoing, it is considered that a compensation fund may be an acceptable practical and efficient solution for the cases of the “orphan” environmental damages, that is, costs that would have been incurred by a liable operator but for its lack (or low level) of financial viability to cover part or all of the costs, is more likely to be acceptable. In this respect, the ELD does not require Member States to remediate environmental damage if the liable operator does not do so. However, at any case it is essential to preserve the preventive and dissuasive action of the liability regime by providing for special grants for safety and prevention in parallel with the implementation of the fund.

4. CONCLUSION

The financial security instruments constitute a very complicated and multifaceted issue. Achieving a harmonization in this field demands a “gradual approach” and a balance between the level of security and the cost thereof[25]. Furthermore, it is left to the government to decide which instruments should be implemented as well as the kind and the level of the regulatory rules. In terms of the EU landscape the biggest issue is related to the lack of standardization among the differentiated national financial system. In this ongoing transitional period regarding the EU financial security ambit the Commission is keen to examine new ideas, such as the establishment of a compensation fund, to further elaborate some proposition and to how they may be eventually come into fruition[26].

The creation of an EU fund or scheme for industrial accidents involving pollution is an idea that has several positive aspects to commend it, for example to cover immediate response measures or “orphan” damages. The existence of funding that would be immediately available to respond to an accident could substantially reduce the consequences and, thus, the total cost of remediating damage and losses resulting from that accident. However, the demanding part of the realization of this idea remains the clear identification and agreement on the purpose and the key elements of the fund or scheme. On this basis, the long experience of the USA financial security market could valuable and helpful [27].

In respect with a potential function of a compensation fund within the ELD some stakeholders [27] raised the issue of whether the fund or scheme would still apply in cases of permit or the state-

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of-the-art defence [28]. It is unlikely, however, that adoption of the permit and state-of-the-art defences by some Member States would cause a problem because it is highly unlikely that either of these defences would apply to a major industrial accident causing pollution. In such circumstances, the operator would almost certainly be in breach of its permit. Further, the state-of-the-art defence would almost certainly not apply to such a pollution incident because the results of a spill or explosion caused by inadvertently mixing two chemicals, etc. would almost certainly be known when it occurred. Finally, one more sticking point concerns the actual efficiency of such a fund that has a predetermined ceiling given the provision for unlimited liability under the ELD.

References

1. The proposal of a Directive on Civil Liability for damage caused by Waste, as presented in 1989, the Green Paper on Remedying Environmental Damage in 1993, the White Paper on Environmental Liability in 2000.
2. Annex II of the ELD.
3. For the background and the history of this provision, «Deal on EU liability regime in the balance», (10 June 2003), ENDS Europe Daily.
4. In particular, 700000 m3 red sludge spilled, 10 persons killed, 286 injuries, 731 claims for damages, 358 damaged properties. For further details on this accident in BIO Intelligence Service et al., 2013. Study to explore the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents, Final report prepared for European Commission, DG ENV,
5. For the main reasons, Bocken, H., 2002, Alternative Compensation Systems for Environmental Liabilities, General Report, AIDA XIth World Congress, New York, 21-25 2002, 5.
6. Bergkamp, L., Herbatschek, N., Jayanti S., 2013. Financial Security and Insurance, in Bergkamp, L. and Goldsmith, B. (eds), The EU Environmental Liability Directive: A Commentary, 124
7. The financial security can be established *ex ante*, before environmental damage occurs, or *ex post*, after damage has been done.
8. A detailed analysis of each financial instrument in Munchmeyer, T., Fogleman, V., Mazza, L., Mudgal S., 2009. Implementation Effectiveness of the Environmental Liability Directive (ELD) and related Financial Security Issues. Bio Intelligence Service, Report for the European Commission (DG Environment), 68-73.
9. Bergkamp, L., Herbatschek, N., Jayanti S., 2013. Financial Security and Insurance, in Bergkamp, L. and Goldsmith, B. (eds), The EU Environmental Liability Directive: A Commentary, 138.
10. By way of illustration, there countries -like Germany- which have a long history of building insurance products for strict liability legislation. At the same time, there are countries –like France, Italy and Spain- that are presenting a significant on-going development by covering numerous environmental risks, as well as countries –like UK- which based on private markets that still assess potential for growth but function well upon demand. However, there are also countries –like Romania or Latvia- still experiencing difficulty with liability legislation and growth of insurance products.
11. Report from the Commission to the Council, the European Parliament, the European Economic and Social Committee, and the Committee of the Regions, under the Article 14(2) of the Directive 2004/35/EC on the environmental liability with regard to the prevention and remedying of environmental damage COM(2010) 581 final.
12. Article 16 of the ELD.
13. Short analysis for each of these countries in BIO Intelligence Service et al., 2012. Study to explore the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents, Final report prepared for European Commission, DG ENV, 32-33.
14. Bergkamp, L., 2005. The European Environmental Liability Directive and its Effects on Industry and the Economy, in R. Mallenbegh, Aansprakelijkheid voor schade aan de natuur, 117.
15. Priest, G.L., 1987. The current Insurance Crisis and Modern Tort Law, Yale Law Journal, 1521.
16. Spanish FSM Law, Art. 26.
17. Spanish FSM Law, Art. 28.
18. Spanish FSM Law, Art. 28(b).

ISBN: 978-960-6865-94-7

19. F. Millet, F., Heuzé, V., 2006. Les Fonds d'indemnisation et l'assurance, in G. Viney, G.. Dubuisson, B.(dir.), Les responsabilités environnementales dans l' espace européen. Point de vue Franco-belge, Bruylant/LGDJ, 482
20. Moussoux, Y., 2012. L'application du principe du pollueur-payeur à la gestion du risque environnemental et à la mutualisation des coûts de la pollution, Lex Electronica, vol. 17.1, 14-15.
21. Bocken, H., 2006. Financial Guarantees in the Environmental Liability Directive: Next Time Better, European Environmental Law Review, 149.
22. BIO Intelligence Service et al., 2013. Study to explore the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents, Final report prepared for European Commission, DG ENV.
23. A dam wall on one of the red mud ponds at the factory collapsed, resulting in around one million cubic metres of red sludge and alkaline water spilling from the reservoir. A one to two metre high wave of toxic waters and sludge killed ten people, injured several hundred more, destroyed over 300 homes, contaminated a thousand hectares of land, including 400 hectares of agricultural land, and polluted the Torna Creek and other local waterways. See also, "Lessons learnt from accidents", Conference in Aix en Provence 2011, http://impel.eu/projects/lessons-learnt-from-accidents-conference-in-marseille-2011/; Justice and Environment (2011) *The "Kolontár Red Mud Case": Environmental Liability*, 2011 Case Study, www.justiceandenvironment.org/_files/file/2011%20ELD %20Kolontar.pdf and *Massive alumina red sludge release after the failure of a containment dam*, 4 October 2010, Kolontar, Hungary, www.aria.developpement-durable.gouv.fr/.../fd_39047_kolontar_ang.pdf.
24. Submission by Hungary to the Environment Council of 19th December 2011, (ST 18596/11).
25. Bergkamp, L., Herbatschek, N., Jayanti S., 2013. Financial Security and Insurance, in Bergkamp, L. and Goldsmith, B. (eds), The EU Environmental Liability Directive: A Commentary, 123.
26. Bocken, H., 2009. Alternative Financial Guaranties under the ELD, European Energy Law Review, 166.
27. G.P. Macey, G.P.,Cannon, Z. J.(ed.), 2007. Reclaiming the Land: Rethinking Superfund Institutions, Methods and Practices, Springer, Fogleman, V., 1992. Hazardous Waste Cleanup, Liability, and Litigation: A Comprehensive Guide to Superfund Law, Quorum Books, Gerrard, M.B., 2007. Amending CERCLA: The post-SARA Amendments to the Comprehensive Environmental Response, Compensation, and Liability Act, American Bar Association.
28. BIO Intelligence Service et al., 2013. Study to explore the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents, Final report prepared for European Commission, DG ENV, 38.
29. BIO Intelligence Service et al., 2013. Study to explore the feasibility of creating a fund to cover environmental liability and losses occurring from industrial accidents, Final report prepared for European Commission, DG ENV, 51.

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The implementation of Water Framework Directive and Flood Directive in Greece: Progress and critical review

E. Eleftheriadou[1*], S. Yannopoulos[2]

[1] Department of Environment and Hydroeconomy of Thessaloniki, Region of Central Macedonia, 546 29 Thessaloniki, Greece.
[2] Laboratory of Hydraulics Works and Environmental Management, School of Rural and Surveying Engineering, Faculty of Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
*Corresponding author: Email: e.eleftheriadou@pkm.gov.gr

Abstract

Water policy in Europe is governed by the implementation of two well-known directives: the Water Framework Directive (WFD) 2000/60/EC and the Flood Directive (FD) 2007/60/EC. The present paper focuses on the implementation progress of both Directives in Greece and the compliance they present with the requirements of the European Commission (EC). The current study focuses on certain obligations that the Greek River Basin Management Plans (RMBPs) did not meet, both at the preparatory phase and on the final issue of the plans. Moreover, it is of crucial importance that the application of the FD is in line with WFD in order to improve efficiency. A first point highlighted by the EC, is the fact that a substantial number of differences are observed among the Greek RBMPs. Also, serious drawbacks of the consultation phase are pointed out, while another substantial issue is that climate change has not been taken under consideration.

Keywords: water framework directive; flood directive; river basin management plan; flood risk management plant

1. INTRODUCTION

The transition of the WFD into the Greek legislation was initiated in 2003 (Law 3199/2003) and since then continuous efforts are being made for the fulfillment of the obligations as set in the Directive. Currently, all 14 River Basin Management Plans (RBMPs) of the Greek territory have been adopted in the national legislation, as they were formed after the public consultation process. Nevertheless, serious omissions and drawbacks are observed in the final issues of the plans. The current study focuses on certain obligations that the Greek RBMPs did not meet, both at the preparatory phase and on the final issue of the plans. A first point highlighted by the EC, is the fact that a substantial number of differences are observed among the Greek RBMPs, mainly due to the fact that each plan was assigned to a different contractor. Secondly, serious drawbacks of the consultation phase are pointed out and in general the consultation process is assessed as unsuccessful. Another substantial issue is that climate change has not been taken under consideration and the required specific adaptation measures are not presented in the Program of Measures of the approved RBMPs.

Moreover, in 2007 the FD, which should be applied in line with WFD, came into force in order to improve efficiency, information exchange and achieve common synergies. This has imposed another parameter that has to be faced by the Member States (MSs) during the implementation of the WFD. Undoubtedly, building synergies between the two directives is a rather demanding task without prior experience on it and consequently it has not been addressed adequately yet.

2. IMPLEMENTATION STATUS

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2.1 Water Framework Directive

According to the WFD [1], water resources management should be based on the geographical borders of the natural basins and not on administrative or political boundaries. The new WFD refers to all the types of water (rivers, lakes, coastal) and promotes the concept of Integrated Water Resources Management (IWRM). The application of IWRM entails the investigation of the mechanisms that would bring the necessary balance between development and environmental protection through a decentralized approach based on public participation. The term "integration" refers to all these aspects that should be considered such as different objectives alongside with any social, economic and ecological impacts [2]. The directive sets concrete aims for the environmental conditions with a very specific timetable for their implementation. Also, a new approach to the assessment of water quality is suggested using ecological criteria.

Member States are called to prepare a range of measures and organize them in a Programme of Measures (PoMs) in their RBMPs, which are updated every six years. The European Commission, according to the requirements of article 18 of the Directive, has issued up to now four Implementation Reports, assessing the progress in the implementation of the WFD in all Member States. In 2015, the Commission published the interim report [3] containing a review on the progress in the implementation of the PoMs by the Member States, based on the reports submitted according to article 15.3 of the WFD. The recommendations provided by this report should be adopted during the update procedure by the end of 2015. During this assessment phase, the Commission issued another 5 assessments of RBMPs of the MSs, ~~Member States (Mss),~~ that had not fulfilled their obligation to report in 2012 (Greece, Spain, Portugal, Belgium and Croatia).

The previous Implementation Report was issued in 2012 [4] and included a review on the progress of the RBMPs implementation status. At that time Greece had not fulfilled its obligations regarding the preparation of the RBMPs, as the public consultation process was not finalized at that stage. The European Court of Justice issued two court rulings against Greece; the first in 2008 for failing to submit the reports on the characterization of the River Basins and the second in 2012 for not reporting on the preparation of the RBMPs.

Greece has 14 river basin districts, out of which 5 are transboundary catchments with Albania, FYROM, Bulgaria and Turkey. Currently, the public consultation process has been finalized in all the 14RBs and the RBMPs have been approved and adopted in the national legislation (the last RBMP of the Aegean Islands was adopted on 17/09/2015). However, no efforts were observed for the preparation of common RBMPs for the transboundary catchments in North Greece and the management plans addressed only the Greek territory of the basin. Greece has not adopted yet the 2nd RBMPs.

According to the Commission [5] half of EU surface waters are unlikely to reach a good ecological status in 2015. The 3rd Implementation Report by the Commission [4] warns that good status will not be reached in 2015 for a significant proportion of water bodies, and draws attention that hydromorphological pressures, pollution and overabstraction form the main pressures on water bodies. Nevertheless, one of the main obstacles for achieving good water status is the nitrogen pollution from agriculture, still observed in high levels in European waters. In addition, the uncertainty of the water status in 2012 of over 40% of water bodies and the weakness to establish a baseline for action has a negative effect on the formation of the PoMs.

2.2 Flood Directive

European Commision introduced the FD as a complementary element of the Water Framework Directive (WFD), recognizing that Europe has experienced extreme floods with devastating consequences, combined with the fact that extreme phenomena are more often due to climate change and intense urbanization. It is widely accepted that the WFD does not address efficiently the management of floods, fact that is mentioned in the introductory text of the FD, even if it contains

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some of the fundamental principles of flood management. Hence, the need for a new framework that would address flood management and mitigation provoked the introduction of the FD.

The first requirement of the FD was the preparation of the Preliminary Flood Risk Assessment (PFRA), based on available information on past flood incidents and on predictions about future events, due by the end of 2011 [6]. Moreover, the identification of areas of potential significant flood risks allows Member States to concentrate on certain areas that are identified with flood risk.

In 2010 the FD was introduced in the Greek legislation with a Common Ministerial Decision [7] and in December 2012 the report of the preliminary flood risk assessment was issued according to Article 4 of the FD. The report included maps of all the river basin districts, data collection of historic floods and identification of those with significant adverse impact, taking into account any human losses, the compensation provided and the flooded area [8].

According to the Commission's Report on the implementation of the FD [3], not all Member States have developed new preliminary flood risk assessments, but a few were based on existing studies or have connected new assessments with existing ones. All Member States were required to report to the Water Information System for Europe (WISE) by 26 May 2010 on their administrative arrangements for the implementation of the FD.

The PFRA is followed by the production of flood hazard maps and flood risk maps, by the end of 2013, for the areas identified as areas of potential significant flood risks. In order to achieve effective risk management, the FD will be applied in cycles and at the end of each six-year cycle the Flood Risk Management Plans (FRMPs) should be prepared. The first cycle should be completed by the end of 2015 with the first set of FRMPs and should be coordinated with the implementation of WFD.

According to the Special Secretariat for Water [8] of the Ministry of Environment and Energy, the remaining flood hazard maps for the RBD GR12 (Thrace) would become available by the end of October 2015, together with the rest of the APSFRs (Areas of Potentially Significant Flood Risk). Also, flood risk maps were due by the end of 2015, according to the timetable of the 5 projects related to the Floods Directive implementation in Greece which are underway.

The European Commission acknowledging the importance of the preparation of reliable flood maps issued in 2007 the "Handbook on good practices for flood mapping in Europe" [9]. According to this document, flood maps form the basis for the management of flood risks and they form a prerequisite for achieving effective and efficient flood management. The status of flood mapping in Europe is described in a document prepared for the 2015 EU Water Conference [10], reporting on the progress of Member States on flood mapping by December 2014, where information is missing from Bulgaria, Greece, Malta and Portugal. Moreover, another European initiative was launched between 2004-2007, aiming on flood forecasting, under the title: "European Exchange Circle on Flood Forecasting" [11]. During this period, forecasting methods were assessed in different areas and priority actions were proposed in the produced report "Good Practice for Delivering Flood-Related Information to the General Public" [12].

According to the FD, Member States should have completed the Preliminary Flood Risk Assessments (PFRAs) and Flood Hazard Risk Maps (FHRMs) by 22 December 2011 and 22 December 2013 respectively. According to the **"**European Overview Assessment of Member States' reports on Preliminary Flood Risk Assessment and Identification of Areas of Potentially Significant Flood Risk", issued in September 2015 by the Commission [13], the majority of the Member States have completed the PFRAs according to Article 4, while only a few states having completed the FHRMs according to Article 13.1b.

3. EVALUATION OF THE IMPLEMENTATION PROGRESS

3.1 Water Framework Directive

According to the WFD, the Member States sharing basins ought to co-ordinate their efforts in order to achieve an integrated management of water resources with the preparation of international RBMPs. Accordingly, the FD highlights the need for cooperation among countries and Member States shall ensure that exchange of relevant information takes place between the competent authorities concerned during the preliminary flood assessment. Up to now, Greece has failed to cooperate with the neighbor countries for a number of issues, one of them being the fact that three out of the four neighboring countries are not part of the European Union.

Regarding the adopted PoMs by the Member States, the Commission concluded that in many cases, the planned measures are not based on the current status of water bodies or on the pressures identified in the RBMPs, but it is observed that decisions on the PoMs were made based on existing structures already in place or on the feasibility of certain actions.

The sole application of the WFD is not sufficient for the achievement of good water status, but there are also a number of other Directives, such as the Urban Waste Water Treatment Directive (91/271/EEC), the Nitrates Directive (91/676/EEC), the Directive on Sustainable Use of Pesticides (2009/128/EC), and others, that should be taken into account during the preparation of the RBMPs.

A common omission observed in most RBMPs is the fact that the environmental needs of water are not addressed adequately. In most cases, only the minimum flows that should be maintained are considered, while other important factors are missing, such as flow frequency, duration and timing. All the above factors should be used in order to ensure environmental sustainability and the ecosystems' health.

The Greek RBMPs were assessed by the European Commission and a report was issued [14] that highlighted the following issues:

- The first and one of the main drawbacks that is observed from the first steps of the Directive's implementation is the delay in meeting the deadlines. The Greek RBMPs were delayed due to a number of factors, as insufficient administrative structures and time-consuming legislative procedures. Subsequently, delays are observed inevitably in the revision of the plans and in the implementation of the PoMs that was due by the end of 2015.
- A crucial issue affecting directly the quality of the RBMPs is the lack of reliable data sets in line with the WFD requirements. The Greek case is characterized by an old monitoring network with incomplete data series. Moreover, the absence of a responsible authority and the involvement of various bodies (national meteorological institute, universities, research centers and many others) in data collection and acquisition resulted in fragmented data sets and often not accessible to the general public. Hence, the unreliable data affected the water characterization as it is based on limited data, while the Commission considers significant the uncertainty derived by the data quality and concludes that the necessary transparency in classification of the water bodies is missing.
- The National Monitoring Program was defined in the Greek Law in 2011 (Common Ministerial Decree 140384) and it was due to provide the first monitoring results at the end of 2013. It is anticipated that the implementation of this program will provide reliable data according to the requirements of the WFD for the proper characterization of the water bodies.
- The economic analysis of water presents variations across the river basins, mainly due to missing information.
- The main responsible authorities for the implementation of the WFD are the Decentralised Administrations (DAs), while the general monitoring is supervised by the Special Secretariat of Water (SSW) at the Ministry of Environment and Energy. However, during the first round of the RBMPs the DAs did not undertake the drafting of the plans, but the SSW run this procedure with the contribution of external contractors.

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- Public consultation was applied according to the Greek Ministry of the Environment and a number of consultation workshops took place, but it is not clear whether the comments received were taken under consideration during the finalization of the drafts RBMPs.
- Reports from many of the consultation workshops show that the involvement of stakeholders was not as active as it was anticipated and there was limited public participation. In general, the Commission does not consider the public consultation process that took place, as successful.
- Concerning the transboundary catchments in North Greece, no common RBMP was submitted. The only other Member State is Bulgaria that shares with Greece Strimonas, Nestos and Maritsa River. Bulgaria had already submitted its RBMP for Strimonas River and Nestos River, before Greece, while Evros/Maritsa River is shared with Turkey as well, which is not a Member State and is not obliged to submit RBMPs.

3.2 Flood Directive

The FD came into force as a complementary part of the WFD concerning flood management and therefore their implementation should be coordinated. The 4th Report of the Commission [3] includes also an assessment of the FD, as it is recognized that only through synergies flood management can be efficiently implemented.

The most crucial factor that has been omitted in the flood risk assessment procedure is the incorporation of climate change and its effects on flood magnitudes and frequencies. According to the report [3], only one third of the Member States have considered the impact of climate change in their assessment. In addition to climate change, other factors as well, such as socio-economic developments that might alter flow regimes, or increase flood prone areas. Sixteen of the 23 MSs have reported on information on climate change in their assessments of flood risk, while only 11 MSs have considered long term developments, other than climate change, but the methods used were unclear.

In 2012, the Commission issued a Report on the information reported by MSs on their PFRA and Identification of Areas of Potentially Significant Flood Risk [15]. The report addressing Greece's progress was based on the information uploaded in WISE (Water Information System Europe). The main outcomes of the Commission's report are:

- Greece has applied Article 4 on the Preliminary Flood Risk Assessment.
- During the PFRA, 297 historic floods have been considered as significant, but no data exist for the majority of them.
- The procedure for the identification of areas where flooding can occur was realized based on geomorphological criteria, such as the slope (threshold of less than 2%) and areas of alluvial deposits, and on historical floods.
- As in the majority of MSs, Greece did not take into account long term developments that would affect flood risk assessment. The only exception was the urban and tourism expansion that was considered, but does not comply with the required level of analysis.
- The FD implementation should be run at a regional level and regional authorities, especially the decentralized administrations, are responsible for the overall management. However, the PFRA in Greece was realized centrally by the Ministry of Environment and Energy.
- Various comments are made on the mapping procedure. The GIS viewer is commented as it considered not very user-friendly as it combines many different topics. Moreover, the structure of the maps is characterized as very complex and not structured according to the APSFRs.

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4. CONCLUSIONS AND RECCOMMENDATIONS

The analysis of the implementation stage and the Commission's Report can provide useful conclusions that could put forward the further implementation steps. One of the main issues of the WFD's implementation and a crucial factor for the achievement of the Directive's goals is the PoMs proposed in the RBMPs. The efficiency of the MSs' PoMs depends on an accurate assessment of pressures and impacts and of the current water status. In case of improper assessments, then the whole RBMP is in risk of failure, as the proposed measures will be based on unrealistic data.

Another technical issue that holds an important role in the success of the RBMPs is the monitoring of the water bodies. Sound monitoring provides a safe base for assessing impacts and building concrete measures that would bring the desired results. Thus, the monitoring network should be enhanced and especially for the priority substances of surface waters. Moreover, a common pressure in most MSs is the diffuse pollution caused by agricultural activities. It is a general remark, that MSs should strengthen their measures in order to confront this issue.

The primary goal in each RBMP is the achievement of good water status through the implementation of the PoMs. However, the efficient design of the PoMs requires a selection of the most cost effective measures that will succeed in the transition of the current water status to "good status". A cost effective analysis of the proposed measures is necessary in order to acquire a better understanding on the time and costs needed to achieve the objectives.

Moreover, great attention should be drawn on water abstractions and the relevant legislation that cover existing abstractions. Recently in Greece, a new legislative framework (Common Ministerial Decision 150559/2011) gave the opportunity to existing water abstractions, independently of their legal status, to continue their functionality as long as there is no change of the abstracted volumes. This measure was adopted in the whole country, without taking into account special conditions or needs of each RBD. It is also commented by the Commission that existing water rights should be reviewed and if necessary updated in order to ensure compatibility with WFD requirements. In addition, the link between water quantity and quality should be investigated further and strict measures should be put in place concerning water abstractions and flow regulations.

The ecological flows should be adopted according to official guidance (Guidance Document n.31) and specific measures should be in place for protecting these flows and to ensure environmental sustainability especially for vulnerable areas.

The pricing of water resources is a prerequisite of the WFD for all sectors. In Greece, the pubic consultation has been completed in the summer of 2015, and the implementation of water pricing should be done within the year 2016. Hence, there are no results yet that could be discussed, but the Commission places great emphasis on the adequate pricing of water resources, especially on the agricultural sector.

It should be noted that in spite the difficulties and the incomplete implementation of the FD, for the first time the MSs are facing flood issues under the same framework in order to fulfill the Directive's goal of preventing social, economic and environmental damage from flooding. Another important change is the fact that in addition to flood protection, MSs are also focusing on prevention and awareness. The tools produced during the FD's implementation, such as flood hazard maps and flood risk maps, can be used by the responsible authorities for preparing measures towards the reduction of flood risks.

Another issue, that had not yet been confronted adequately, is the preparation of common plans in transboundary catchments. The European Union has repeatedly included in various Directives general principles for achieving transboundary cooperation, while there are European examples of good practice such as the Rhine and the Danube. Yet, transboundary cooperation on a regular basis is not observed, in most cases for various reasons such as the heterogeneity of data, different

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standards, lack of political will and inadequate efforts across borders to deal effectively with managing risks. Funding interregional projects can form the basis for scientific and political cooperation, but such efforts often end with the project's deadline and it is quite rare to achieve a follow-up of the cooperation paths achieved during the project.

Especially in Greece, where roughly 25% of the country's renewable resources are "imported", transboundary water resources constitute a major asset for the country and introduce high uncertainty for the country's imported water. Although many efforts have been made and many bilateral memoranda of co-operation have been signed between Greece and the neighboring counties, the process of applying common management plans has not yet been implemented. Co-operation until now, took place through fragmented measures, ignorance of the local needs, giving emphasis on securing users rights rather than treating transboundary rivers as a unity, which should be jointly protected and managed.

Concluding, the efficient implementation of both Directives is highly based on the administrative capabilities of ensuring that cooperation paths remain open among authorities at various levels. The responsible bodies implementing all the plans should be decentralized and based at each RBD. It is highly recommended to rely on existing structures that have proven to be successful and especially for the efficient implementation of the FD, the MSs should take advantage of the experience gained by the implementation of the WFD.

References

[1] European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, *OJ L 327*

[2] Biswas A.K., 2004. Integrated Water Resources Management: A Reassement. *Water International*, **29 (2)**, 248-256

[3] European Commission, 2015. The Water Framework Directive and the Floods Directive: Actions towards the 'good status' of EU water and to reduce flood risks, 4th Implementation Report, *Communication from the Commission to the European Parliament and the Council*, 09.03.15, Brussels

[4] European Commission, 2012. River Basin Management Plans, 3rd Implementation Report, *Communication from the Commission to the European Parliament and the Council on the Implementation of the Water Framework Directive*, 14.11.12, Brussels

[5] European Commission, 2012. A Blueprint to Safeguard Europe's Water Resources. *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions*, 14.11.02, Brussels

[6] European Commission, 2007. Directive 2007/60/EC of the European Parliament and of the Council of 23 October 2007 on the assessment and management of flood risks, *OJ L 288*

[7] Ministry of Environment, Energy and Climate Change (MEECC), 2010. Common Ministerial Decision No. 31822/1542/E103, 2010. Assessment and Management of Flood Risks in compliance with Directive 2007/60/EC of the European Parliament and of the Council of 23 October 2007. Greek Republic.

[8] Ministry of Reconstruction of Production, Environment and Energy (MRPEE) (*now called Ministry of Environment and Energy)* - Special Secretariat for Water, 2012. The Implementation of Directive 2007/60/EC: *Preliminary Flood Risk Assessment*. Athens

[9] EXCIMAP (European Exchange Circle on Flood Mapping), 2007. Handbook on Good Practices for Flood Mapping in Europe. (accessed at: http://ec. europa.eu/environment/water/flood_risk/ flood_atlas /pdf/handbook_goodpractice.pdf, January 2015)

[10] European Commission, 2014. Member States' Examples of Flood Hazard and Flood Risk Maps. (accessed at: http://ec.europa.eu/environment/water/flood_risk/pdf/MS%20 examples.pdf, January 2015)

[11] UNECE (United Nations Economic Commission for Europe), 2009. Transboundary Flood Risk Management, Experiences from the UNECE region. UN, New York and Geneva.

[12] EXCIFF (European Exchange Circle on Flood Forecasting), 2007. Good Practice for Delivering Flood-Related Information to the General Public. (accessed at http://publications.jrc.ec.europa.eu

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/repository/bitstream/111111111/4752/1/7224%20-%20EUR%2022760%20FINAL%20-%20FF% 20 guide_plus_annexes. pdf, March 2015)
[13] European Commission, 2015. European Overview – Assessment of Member-States' reports on Preliminary Flood Risk Assessment and Identification of Areas of Potentially Significant Flood Risk, Final Report (http://ec.europa.eu/environment/water/flood_risk/pdf/ pfra_reports /EU%20PFRA %20Overview%20Report.pdf, accessed at March 2016)
[14] European Commission, 2015. Report on the Implementation of the Water Framework Directive River Basin Management Plans, Member-State Greece, *Commission Staff Working Document*, 09.03.15, Brussels
[15] European Commission, 2012. Assessment of data and information reported by Member States on their Preliminary Flood Risk Assessments and identification of Areas of Potentially Significant Flood Risk under the Floods Directive (http://ec.europa.eu/environment/water/flood_risk/pdf/ pfra_reports /PFRA%20Report%20-%20EL.pdf, accessed at March 2016)

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The legal point of view of forest road construction

A. Douka[1*], V. Giannoulas[2]

[1] Faculty of Law, Aristotle University of Thessaloniki, 541 24, Thessaloniki, Greece
[2] Department of Forestry and Natural Environment, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece
*Corresponding author: Email: sissi010591@hotmail.com

Abstract

A strategy for the sustainable development of mountainous areas necessarily involves the exploitation of the natural environment. Any intervention in the natural environment has to comply with the basic established principles of forestry and environmental law (sustainable management of forests). The absence of a comprehensive legal framework in Greece, which describes with clarity, sufficient detail and accuracy the technical specifications, which must be fulfilled by environmental commitments call the environmental compatibility of projects into question. Therefore, the integration of objective, scientific criteria in the existent legislation, which ensure a minimum environmental protection from the multiple implications of the proposed forest road constructions is essential. Aim of the present study is the examination and evaluation of the objectivity, coherence and completeness of the legal framework of developing environmental commitments of forest road construction, in comparison with European standards.

Keywords: environmental commitments; forest road construction; legal framework

1. INTRODUCTION

The subject of this study is the presentation of the current legislative framework in Greece regarding the development of environmental commitments for forest road construction, the identification of its deficiencies and the determination of the scientific environmental criteria, which need to be taken into consideration by researchers. A comparative overview of the Swiss model was considered essential for the determination of specific and not general environmental criteria. The Swiss model was specifically chosen, because Switzerland was one from the first countries, which adopted a constitutional obligation for the protection of environment in 1971 [1]. On the contrary, the heads of government of the former European Economic Community declared an intent to adopt a common environmental policy in 1972. A proposed (rather than a preliminary) draft EIA Directive was published in 1980 by the Commission of the European Communities [2].

By definition, a forest road is an artificial strip of land, which has taken shape from the viewpoint of geometrical features and quality of pavement in order to serve the demands of users for forest protection [3]. The opening up of a forest road has to balance between financial and social outputs and sustainable development. Despite the benefits, the construction of forest road is accompanied by negative impacts on the environment. These may be defined as changes caused to environmental resources (natural and social), with a temporary or permanent character in respect of the time horizon within which these changes take place [3].

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2. MATERIALS AND METHODS

The protection against the alterations caused to the natural environment by the construction of forest roads is regulated by a) environmental law and b) forest protection law.

2.1 Environmental law

According to the Greek environmental law, projects and activities of public and private sector, those construction or operation can provoke implications on the natural environment, are divided into two categories (A and B). Projects followed by significant environmental implications, belong to the first category of projects and they are mandatorily subject to an environmental impact assessment (EIA), which imposes specific conditions and limitations aimed at the protection of the environment [4]. On the other hand, projects followed by local and not significant environmental implications, belong to the second category of projects and they are subject to general requirements, restrictions and specifications [4]. Systematic assessment is not prerequisite for projects belonging to the second category. As result, they are not subject to environmental impact assessments, but exclusively subject to environmental commitments, which are an integral part of the required authorisations for construction, establishment or operation of the project [5].

The procedure of environmental impact assessments for projects in NATURA areas is stricter. Precisely, an indispensable additional condition for the approval of projects of both categories mentioned above is their previous specific ecological assessment, which is a preliminary examination of possible adverse effects. In case of projects belonging to the first category, the specific ecological assessment is part of the EIA. Specific ecological assessment of projects belonging to the second category, which highlight the danger of the protected area, is included as additional condition in environmental commitments following the relevant decision of the regional governor [6].

Forest road construction belongs to the second category of projects and more precisely to the type of projects entitled “land or air transport projects – road construction” [7]. As far as the procedure is concerned, the competent authority for the granting of an authorisation is responsible for ipso jure inclusion of forest road construction in environmental commitments [5].The competent authority in case of forest road construction is the environmental and spatial planning department of the region concerned [8]. Prerequisite is the relevant statement of the developer or the project promoter. Projects not accompanied by an authorisation are included in environmental commitments on responsibility of the competent environmental department of the region [5].

The statement of the inclusion of the project in environmental commitments is accompanied by the following documentation: 1) a concise technical report of the project and other supporting works, 2) mapping of the project and the region of its operation and 3) an opinion by the competent archaeological authority about whether the location of the project is of archaeological interest or not. If the project is located outside of the town plan and outside of agglomerations’ limits, the following additional documents are also required: 1) act of characterization of the area, where needed, according to the provisions of forest law legislation and 2) an opinion of the competent forestry regarding additional environmental commitments about forest protection [9].

2.2 Forest protection law

The opening up of forest roads into forest ecosystems (forests, forest and reforested areas and public areas) is permissible within the terms of the environmental report of the project as well as the terms of the conservation of forest protective characteristics. Environmental criteria which need to be taken into account through the adoption of protective measures are following: non – alteration of the natural environment, protection and recovery of forestry vegetation and creation of new vegetation for operational and cosmetic reasons. Moreover, persons entitled to the opening up of forest roads are obliged to create row trees and straight – line plantations alongside the road, according to the instructions of the competent forestry administration [10].

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2.3 Evaluation of the Greek legal framework of environmental commitments in comparison to the Swiss model

From a scientific perspective, environmental commitments are developed on the basis of descriptive criteria and therefore they involve the risk of presentation of environmental criteria without objectivity. The primary, immediately noticeable and measurable effects are detected by the developer. However, there are also negative spill - over effects, which are not easily noticeable or measurable and as a result not assessed [11].

For these particular reasons, practicable and objective assessment methods of environmental impacts have to be established, in order to define the accurate position of the construction of the project, which ensures its environmental compatibility [12, 13]. At this point, the contribution of a forest expert is crucial. A forest expert, who is responsible for the natural environment, has to examine before the construction of the foreseen project if there is an environmentally compatible area available and provide the relevant instructions [14]. Moreover, the implications of the implementation not only of an individual, but of a whole development project have to be assessed by environmental commitments as an environmental cost [15].

From a legal point of view, the aforesaid authorisations including environmental commitments, are subject to judicial review. The Greek Council of State (Ste) considers that the opening up of forest roads is an exceptional measure acting in the public interest. The necessity of this measure as well as the fulfilling of conditions of sufficient forest protection has to be adequately reasoned [16].

It is important to point out here that, the Greek Council of State (Ste), as far as the examination of environmental impact assessments (EIA) is concerned, appears in the last years very hesitant about the annulment of the decisions of the Minister of Environment, Energy and Climate Change which include EIAs and grant or refuse development consent. Straight evaluation of EIAs as well as their opposition to the principle of sustainable development, as pointed out by the Greek Council of State, are excluded from the Court' s limits of control [17]. This is a usual manoeuvre of Greek Council of State anchored in its inviolable limits of control. The judge of the Council of State is not competent to examine if the facts presented in an EIA respond to reality. The evaluation of facts is only exhausted at an administrative level. The real reason for this kind of weighting between environmental protection and economic development is the financial crisis which plagues Greece in the last years.

Similar approach of the Greek Council of State is also awaited in the case of judicial review of environmental commitments. This is because, in comparison to EIA, environmental commitments refer to projects with less harmful environmental impacts. The attitude of the Greek Council of State is undoubtedly encouraged by the absence of precise, analytical, identified and concrete environmental criteria, which should be taken into consideration by the developer.

The proper evaluation of the environmental commitments of forest road construction prerequisites the objective answer to a number of specific questions by the researcher. Common questions, proposed by the canton of Berne [18] serve as an important guide for the improvement of the Greek legal framework.

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Table 1. Questions according to the proposed work: Roads

Data of the project essential for the developing of environmental commitments	
Purpose of the project and forecast of traffic	
Functionality of the project	Which is the aim of the project (e.g. a new construction, extension etc.)? Which are the problems solved through the construction of the road? Which areas are connected to the proposed project of traffic and which will be built up? Which is the road category planned?
Accompanying measures	Which existing transport installations are organisationally and structurally subjected to interferences? Which is the timetable set out for the implementation of the project?
Traffic	Which is the traffic foreseen on the planned road? Which traffic changes are expected in the rest network? In which way does the overall service of the traffic change? Which kind of cargoes are expected? Are any implications on other means of transport (e.g. public transport, bicycle, aircraft) expected?
Road layout and technical works	
Road layout	Which is the road layout foreseen? Does it correspond to the operation of the road? Are there any other variations available? In which areas are reactions expected? Does the layout satisfy the operation of the road?
Area requirement	Which is the area required for the whole project? Which uses are nowadays being affected?
Connection	In which way will the planned road be connected to the rest transport network? Are there any changes caused to soil surface? Is there any permanent change of soil foreseen on account of dikes? Where will the used material be discarded?
Technical works	Which technical works are designed (e.g. walls, passages, tunnels, soils, bridges)?
Cross section	How many lanes does the road have? Does the cross section satisfy the operation of the road?
Water supply	In which way do technical works and slopes drain? How will storm water be distributed? Where will petrol stations be constructed?
Lightning and ventilation	Is the lightning provided by the road adequate? In which way will any tunnel built be vented?
Planting	In which way will the goal of greening of the area around the road be achieved?
Subsequent infrastructure of the project and adjustments	
Water engineering works	Are any works for temporal or permanent water supply required?
Adjustment of transfer systems	Are any works planned for temporal or permanent diversion of flow for the adjustment of the road?
Auxiliary installations	Which are the auxiliary systems foreseen (e.g. petrol stations, stations for rest breaks etc.)?

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Table 2. Usual conflicts and gained experience

Protection of the nature and landscape	The construction of a new road usually affects harmfully animal, plant habitat and the landscape view. Such implications are caused by the construction itself (e.g. destruction or fragmentation of habitats, vision changes) as well as by the relevant circulation (e.g. noise, pollutants, animal movement).Therefore, the constitution of the landscape and the establishment of new habitats are extremely important.
Agriculture	The construction of a road usually opposes to the maintenance of agricultural land.
Traffic	The environmental impacts of the construction of a road are fundamentally determined by traffic. Consequently, it is an urgent need to forecast the traffic of the purposed road and the other elements affected by road network. It should be noted that more traffic is expected on account of new and updated connections. The cross section and layout of the road network should take into account a stable flow of traffic.
Noise emissions	Along roadsides with heavy traffic noise limits are usually exceeded. Therefore, traffic volume should be foreseen.
Air pollution	According to the atmospheric pollutants caused by traffic, NO_2 emissions increase significantly at speeds above 60 km/h. Emissions caused by secondary materials of nitrogen oxides (ozone, acids) and particles of motor vehicles can also be significant. Given the fact that atmospheric pollutants are not confined at the street level, climatic and meteorological implications are often inevitable.
Soil and water	Due to permanent covering of the upper soil surface of the road, pollutants caused by tyre wear, exhaust gases, lead residues etc. cause to the environment qualitative and quantitative effects on soil and groundwater.

3. RESULTS AND CONCLUSIONS

Due to the fact that the legislative framework of environmental commitments of forest road construction is governed by two different pillars (environment law and forest law), it is not integrated, coherent and complete and as a result the protection of the environment turns out to be insufficient. The procedure of developing environmental commitments is descriptive and restricted at an administrative level. This particularly means that it is exposed at political interests served by the government in force. An independent expert authority, which guarantees objectivity and impartiality is the appropriate to take on the role of issuing authorisation for the opening up of forest roads.

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References

[1] Kloepfer M., 1998. *Umweltrecht.* 2nd ed. C.H. Beck Publishers, Munich.
[2] Wathern P., 1988.Containing reform: The UK stance on the European Community EIA Directive. *Policy Studies Review*, **8 (1)**, 95-104
[3] Doukas A.-K., Drosos V., 2013. *Forest road construction and natural environment.* 1st ed. Tziola Publishers, Thessaloniki.
[4] Art. 3 par. 1 of Law 1650/1986 on environmental protection, as amended by the Law 4014/2011
[5] Art. 4 of Law 1650/1986 on environmental protection, as amended by art.8 of Law 4014/2011
[6] Art. 4 of Law 1650/1986 on environmental protection, as amended by art.10 of Law 4014/2011
[7] Decision of the Minister of Environment, Energy and Climate Change 1958/2012, Off. Gaz. A 209/2011
[8] Art. 2 par. 1 of the Decision of the Minister of Infrastructure, Transport and Networks and the Minister of Environment, Energy and Climate Change 170613/2013, Off. Gaz. B 2505/2013
[9] Art. 4 of the Decision of the Minister of Infrastructure, Transport and Networks and the Minister of Environment, Energy and Climate Change 170613/2013, Off. Gaz. B 2505/2013
[10] Art. 48 of Law 998/1979 on forest protection, as amended by Law 4280/2014
[11] Doukas K., 2004. *Forest construction and natural environment.* 1st ed. Giachoudi Publishers. Thessaloniki.
[12] Becker G., 1995. Walderschließung auf dem Prüfstand. *Allgemeine Forstzeitschrift (AFZ)*, 9, 482 -483
[13] Giannoulas V., Drosos V., Doukas K., 2004. Environmental impact assessments for forest roads in the university forest of Pertouli (Braikou area). *Scientific Yearbook of Department of Forestry and Natural Environment.* Thessaloniki, 549 – 566
[14] Drosos V.,Karagiannis E.,Doukas K.,2014. *Opening-up of forests– Transport of forest products*. 1st ed. Tziola Publishers, Thessaloniki.
[15] Giannoulas V.,Stergiadou A.,Drosos V., 2007. Environmental impact assessments for forest roads in Metsovo. *Integrated Development of Epeiros*. D. Rokos Interdisciplinary research centre of Metsovo Publishers. Athens, 534 – 551
[16] Ste 772/1992 NOMOS Legal Database (https://lawdb.intrasoftnet.com/)
[17] Ste 4491/2009,Ste 613/2002,Ste 3478/2000 NOMOS Legal Database (https://lawdb.intrasoftnet.com/)
[18] Hilfsmittel für Untersuchungen zur Umweltverträglickeit von Anlagen. 1991. Koordinationsstelle für Umweltschutz des Kantons Bern

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Offshore Wind Energy vs. Nature Conservation: the role of Maritime Spatial Planning in striking the balance

A. M. Kitsou [1], V. Vassilopoulou[2]

[1]University of Aberdeen, UK.
[2]Institute of Marine Biological Resources and Inland Waters, Hellenic Centre for Marine Research, PO BOX 712, 19013, Anavyssos, Greece
Email: iriakitsou@gmail.com

Abstract

Focusing on the marine environment, this paper will consider whether the EU's biodiversity protection regime under the Habitats/Birds Directive could restrict the expansion of Offshore Wind Energy (hereinafter OWE) in EU marine areas. Taking into account that the Natura 2000 network already covers a substantial part of the EU territory and is expected to further expand -especially offshore- the potential rejection of OWE development proposals on ecological conservation grounds could compromise both the EU's ability to fulfill its commitment under the Renewables Directive as well as its ambition to reach 80-95% decarbonisation by 2050. Having identified that a risk of constraint on the OWE programme is very likely to arise, this paper will additionally reflect on whether maritime spatial planning could be used as an appropriate legal response, in order to mitigate or even avoid potential risks of conflict between OWE development and biodiversity obligations.

Keywords: renewable energy; biodiversity ; decarbonisation; Habitats Directive; maritime spatial planning;

Introduction

Being a global leader in climate action, the European Union has committed itself to achieving a 20% reduction in greenhouse gas emissions by 2020 compared to 1990 levels [1]. Moreover, it has a political aspiration to move beyond this figure by 2050, aiming at 80-95% decarbonisation below 1990 levels [2]. In reaching these rather ambitious targets, Renewable Energy Technologies (hereinafter: RETs) have a unique and very crucial role to play and this is something the EU is well aware of. As a result, it has further committed itself to a 20% share of renewable energy in gross energy consumption by 2020, and to this end it has adopted legislation [3] that sets mandatory national renewable energy targets for each member state, to ensure that the overall EU target is delivered. Binding national targets are expected to encourage the development and use of new technologies generating energy from renewable sources. Maritime wind energy presents currently a very promising RET, in the sense that it is capable of making a significant contribution to meeting both national renewable energy and climate change obligations. Considering also that the EU possesses abundant offshore wind resources [4], one can imagine how important a part OWE could have in the continent's attempt to escape 'carbon lock-in'.

Barring renewable energy and carbon emissions reduction targets and political goals, the EU places biodiversity protection similarly high in its environmental policy agenda [5]. This is the reason why it established, under the Habitats and Birds Directives [6], a scheme of strict protection of ecologically significant species and habitats throughout Europe. This designated 'network' of

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Special Areas of Conservation (SACs) and Special Protection Areas (SPAs) is likely to operate as the European 'museum of nature'. The choice of the latter phrase is not accidental, since Natura 2000 sites are intended to give shelter to natural habitat types and vulnerable species, which would otherwise be victimised by human activities. Therefore, any developments or other uses likely to impact upon a site's ability to deliver its ecological objectives need to be very carefully considered and, where possible, avoided.

But what happens when a likely harmful development serves more than just political and profit maximising purposes? What if it forms an indispensable part of a collective effort to combat an alarming environmental problem (i.e. climate change) calling for urgent action? Could that be a sufficient justification for conservation interests to be 'overridden'? Or are provisions aimed at biodiversity protection 'sacrosanct', even if such a thing implies that policies intended to tackle climate change will be hindered [7]? Under which circumstances does this alleged 'conflict' materialise and, to the extent that this risk of conflict does occur, how can it be addressed?

Protecting biodiversity in EU marine areas

Despite the undisputed regulatory value of the Birds and Habitats Directives, their influence within the marine environment has historically been very limited [8]. Indeed, in contrast to the creation of a large terrestrial network of protected species and habitats across the EU, the vast majority of member states have proven to be very slow in the designation of marine Natura 2000 sites [9]. Nevertheless, things have begun to change (relatively) recently, with the EU exhibiting a remarkable interest in marine environmental affairs [10]. Fully consistent with this trend, the advancement of the Natura 2000 network within inshore and offshore areas has been given an increasing emphasis. As a matter of fact, in recent years, EU Member States such as Denmark, Poland, Estonia, the Netherlands and Belgium have designated a significant number of marine Natura 2000 sites in their respective waters, with Germany being currently ahead of all by having designated almost 45% of its marine space as Natura sites [9, p. 375]. This move towards a greater engagement with marine biodiversity concerns can be justified on several grounds, the most important of which is the unpleasant recognition that ecosystem degradation will not be halted, unless some serious action is taken. The reality is that, despite EU's eagerness to prevent habitat and species loss, the Biodiversity Action Plan targets for 2010 were missed [11]. A report issued by the European Environment Agency found that only 17% of habitats and species and 11% of key ecosystems protected under EU legislation were in a favourable state in 2010 [12]. This was the motivation for additional measures to be adopted. As a consequence, the European Commission in its 3.5.2011 Communication 'Our life insurance, our natural capital: an EU biodiversity strategy to 2020' took nature conservation goals two steps further through the inclusion of a 2020 headline target as well as an ambitious 2050 vision [13].

Marine Biodiversity Protection and OWE development: a legal compromise or a deadlock?

3.1 Introduction

Having adopted more ambitious biodiversity and renewable energy targets than most of its counterparts, the EU is very likely to be an important testing-ground for potential conflicts between these two policies [7, p. 1197]. Bearing this in mind, two questions can be posed:

1) To what extent does (or does not) the EU nature conservation regime obstructs the attainment of renewable energy legal and policy objectives?

2) Conversely, is there a risk for biodiversity protection to be compromised, in the effort to reach renewable energy targets?

3.2 Avoiding deterioration and significant disturbance

Article 6(2) of the Habitats Directive imposes upon states a general duty to avoid the human

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induced deterioration and/or disturbance of the protected sites. It is in this context that environmentally destructive activities and practices come into picture. In fact, in its 2007 guidance on the establishment of the Natura 2000 network in the marine environment, the European Commission has cited several examples of human activities, which, if not properly handled, are very likely to cause deterioration and/or significant disturbance of the SAC/SPA [10, pp. 91-104]. Being part of that catalogue, OWE production is also expected to adversely affect the conservation status of the protected species and habitats, as a result of its various negative environmental ramifications (i.e. bird collisions, underwater noise, electromagnetic fields etc.) [14]. Should it be proven that the detrimental effects of a proposed OWF are capable of either deteriorating or significantly disturbing the individual conservation objectives of a particular SAC or SPA, it is incumbent upon states to take all appropriate steps to prevent this situation from occurring. This could involve the mitigation of the damaging impact or, where mitigation is not feasible, the rejection of the OWE development proposal (see art. 6 par. 3 and 4 of the Habitats Directive). Taking into account that offshore wind constitutes one of the most valuable renewable energy sources, the non-authorisation scenario could, under very specific circumstances, compromise the EU's ability to achieve its desired renewable energy/decarbonisation targets.

3.3 The way to authorisation (or maybe not?)

According to article 6(3), any plan or project *'likely to have a significant effect'* on a Natura 2000 site has to be made subject to an Appropriate Assessment (hereinafter: AA) of its implications for the site concerned. Given the magnitude of OWE installations' negative environmental consequences, it will often be the case for Offshore Wind Farms (hereinafter OWFs) proposed to take place within or close to Natura 2000 sites to undergo an AA. In light of the conclusions of the AA, competent national authorities will authorise a plan/project, whenever they have established with certainty that it will not adversely affect the integrity of the site concerned. In other words, only where no reasonable scientific doubt remains as to the absence of such an effect can such an activity go ahead.

The requirement for 'no reasonable scientific doubt' sets a considerably high threshold, which many projects (and plans) will not be able to pass [7, p. 1198]. This was the case with several OWFs that were initially proposed to take place within or close to SPAs. One of the most indicative examples is the London Array offshore wind farm [15], which is located off the coasts of Kent and Essex in the outer Thames Estuary SPA. Whilst phase 1 of the project was granted permission and development proceeded (175 turbines were installed, which covered an area of almost $40km^2$ and generated up to 630MW of power) [16], phase 2 expansion plans were abandoned, because of concerns over their impact on the red-throated diver, a migrating seabird that overwinters in the -designated as an SPA- area around the wind farm [17]. As it was explained, it would have taken until 2017 (almost 3 years) to assess whether the impact of the additional turbines on the protected bird species would be acceptable [17]. Apart from the London Array case, other OWE development proposals that were not also given the green light, by virtue of their uncertain impacts on bird populations protected under the 2009/147/EC Directive, have been the Sikka I-Bajda (Malta) and the Cirrus Shell Flat Array (United Kingdom) offshore wind farms [18, 19]. In the former case the proposal was permanently aborted [20], whereas in the latter a suggestion was made for the project to be relocated in an area appearing to be of less ecological importance (finally, the project was cancelled due to aviation safety reasons) [19].

3.4 OWE vs. Biodiversity: the potential conflict

Remarkably, apart from the Cirrus Shell Flat Array OWF (for which an alternative location was found) the other two OWF proposals fell through, following a negative assessment of their implications for the SPAs concerned. These cases, along with some other renewable energy development proposals that were not approved on biodiversity protection grounds (e.g. Vlakte van

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de Raan OWF [21] in Belgium), seem to be setting an unwanted precedent in the promotion of renewable technologies, which could act as a barrier to the overall effort to halt climate change. In layman's terms, there is a risk that the strict nature conservation regime may lead to the withdrawal of many large renewable energy projects that were expected to make a significant contribution to the decarbonisation struggle. Although the extent of the barrier is not something we can establish now, it is to be recognised that, in view of the demanding future policy aspirations of the EU, a risk of constraint on the OWE (and Renewable Energy in general) programme is very likely to arise.
Things become even more complex when considering that the expansion of the Natura 2000 network (especially offshore) is very likely to take place as a meaningful response to the desired 2020 and 2050 biodiversity goals. Given that the Natura 2000 network covers almost 18% of the EU's entire land area and 'significant additional marine areas' [7, p. 1199], a further increase in its size could, in certain cases, give rise to conflicts between overlapping, yet distinct, interests. That said, the anticipated designation of a substantial number of marine protected sites could inhibit the expected growth of the EU's OWE programme, in the sense that OWFs, proposed to be located within or close to SACs or SPAs, could run the risk of being rejected, after having been made subject to an appropriate assessment of their implications for the sites concerned. Furthermore, due to current technological restrictions, OWF development is confined to a limited geographical space. Provided that a substantial part of this space is incorporated into the Natura 2000 network, the risk of constraint on OWE growth becomes even more evident. Bearing in mind that the exploitation of offshore wind resources is expected to be on top of EU's list of priorities towards tackling climate change, the potential compromise of the OWE programme could also jeopardise the longer-term decarbonisation vision.

Maritime Spatial Planning: an adequate response?

Given that the goal should be the reconciliation -and not the prioritisation- of nature conservation and decarbonisation policies, an approach, capable of predicting and preventing potentially competing interests, could be the most efficient means of achieving this. This is the case with integrated maritime spatial planning (hereinafter: MSP), a relatively new concept [22], which has attracted the attention of governmental, intergovernmental and regional institutions, environmental NGOs and scholars across the world. Given the anticipated rise in the number of OWFs, the considerable expansion of the Natura 2000 network at sea and the existence of various other offshore uses that require adequate siting within a finite physical space, conflicts among OWE and nature conservation policies will become insurmountable, unless they are *a priori* addressed.

Avoiding the conflict in the first place -in a way also that does not undermine any of the competing interests- necessitates clear objectives and thorough planning. In this respect, MSP's ability to rationally organise the marine space could be of great value. Following the example of Germany and the Netherlands, one possible way to proceed could be to exclude OWF development from Natura 2000 sites [23]. This approach has the merit of keeping vulnerable marine ecosystems intact, while simultaneously allowing for OWE deployment in the rest of the offshore space. However, it is highly questionable how this is going to work in view of the expected proliferation of marine SACs/SPAs, in conjunction with the projected increase in the number of OWE installations. At this point it is important to highlight that MSP's role is not solely confined to the spatial distribution of marine uses. Instead, according to Douvere, MSP enables guidance of single-sector decisions toward holistic management of the ocean, thereby enhancing synergies and preventing conflicts both among uses and between uses and the marine environment [24]. Remarkably, Douvere seems to imply that 'nature conservation' does not fall under the concept of 'uses'. Indeed, the debate on whether 'nature conservation' should be regarded as a marine use or as the major policy objective underlying the entire MSP process is far from over [25].

A possible answer could be found in the text of the MSP Directive [26]. More specifically, article 5(1) of the Directive states that member states shall apply an ecosystem-based approach,

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when establishing their national marine spatial plans. As Qiu and Jones point out, a true 'ecosystem-based MSP' is based on the idea of hard sustainability, which, on its part, builds on the view that natural capital must be preserved and enhanced, because the functions it performs cannot be adequately replicated by man-made capital [22, p. 183]. This means that ecosystem goods and services form the foundation of the MSP process, and should they collapse, socioeconomic sectors that depend on them will inevitably collapse as well. On the other hand, most national MSP initiatives (e.g. Belgium, Germany, Portugal etc.) follow what Qiu and Jones describe as 'integrated-use MSP', based on soft sustainability. Within this context, nature conservation is considered just one of the pillars upon which MSP builds – the rest being fisheries, energy, tourism, shipping etc. Accordingly, the main goal of the planning process is to reinforce the overall economic growth associated with marine sectors in a sustainable manner. Given that the soft sustainability concept allows for mutual compensations between natural and man-made capital, there is the possibility that socioeconomic development may overshadow ecosystem preservation. If this is the case, ecosystems goods and services might irreversibly collapse and, as a consequence, related socioeconomic sectors will also come to an end, leading to the replacement of soft sustainability by unsustainable development [25].

The risks inherent to integrated-use MSP make it imperative for EU member states to follow a holistic and integrative ecosystem-based approach when implementing their respective marine spatial plans. In this context, nature conservation is perceived as the overarching policy objective of the MSP process, and is placed above use related interests [27]. Provided that MSP is capable of incorporating and addressing 'changes' in marine ecosystems and human uses over time [28], potential conflicts among the various sector-based policies will be substantially decreased. In accordance, OWE deployment will be harmonised -and not at odds- with biodiversity protection.

Conclusion

In his essay '*The Habitats Directive: Nature and Law*', Paul Stookes reached the conclusion that 'there is an inherent conflict within the (Habitats) Directive between habitat and species conservation and improvement and the pursuit of plans and projects' [29]. Following this assessment of his, it is clear that two variables are determinative of the alleged conflict's magnitude: the need to protect and enhance biodiversity and the demand for economic and social development. Up until now, experience has shown that the rhetoric of nature conservation was easily 'overridden' in the face of financial and other industrial interests, as a result of the lax interpretation of the provisions of article 6 HD. Having acknowledged its complete failure to adequately preserve its natural heritage, the EU committed itself to a future of more meaningful biodiversity protection. However, the 'side-effects' of this aspiration could potentially become devastating for another EU environmental policy sector, that of climate change mitigation. Indeed, the stricter application of the Natura 2000 regime within a substantially expanded network of protected areas could necessitate the rejection of many large offshore wind –and renewable- energy development proposals, which, on their part, are expected to play a central role in achieving the EU's ambitious 2020 and 2050 energy and emissions reduction targets. Being too early to conceive the full extent of this conflict, it is difficult to come up with the appropriate solutions of dealing with it. Given that the goal should be the reconciliation -and not the prioritisation- of nature conservation and decarbonisation policies, and that the existing regulatory mechanisms cannot be trusted in achieving this, new, unexplored (or less explored) regulatory tools need to be found and implemented. This has been the motivation for the EU to enact legislation that creates a common framework for MSP in Europe. Provided that all coastal member states engage in a proactive and responsible implementation of their marine spatial plans, following a meaningful ecosystem-based approach, potential conflicts will be avoided and synergies will be created both among uses and between uses and the marine environment. So far, MSP provides the EU with a unique opportunity to deliver sustainable governance of its marine areas. Whether it will succeed in this only time will tell.

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References

[1] Commission, ‘20 20 by 2020 – Europe’s climate change opportunity’ (Communication) COM (2008) 30 final.

[2] Commission, ‘Energy Roadmap 2050’ (Communication) COM (2011) 885 final, p. 2.

[3] Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC [2009] OJ L 140/16 (Renewable Energy Directive).

[4] EWEA, ‘Oceans of Opportunity: Harnessing Europe’s largest domestic energy resource’ (*EWEA Report*, September 2009), p. 7.

[5] Commission, ‘Wind energy developments and Natura 2000’ (*European Commission*, 2011), p. 16.

[6] Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora [1992] OJ L 206 (Habitats Directive); Directive 2009/147/EC of the European Parliament and of the Council of 30 November 2009 on the conservation of wild birds [2009] OJ L 20 (Birds Directive).

[7] Jackson A. 2011, Renewable Energy vs. biodiversity: policy conflicts and the future of nature conservation. *Global Environmental Change*, **21**, 1195.

[8] Caddell R., ‘The Maritime Dimensions of the Habitats Directive: Past Challenges and Future Opportunities’ in Gregory Jones (ed.), *The Habitats Directive: A Developer’s Obstacle Course?* (Hart Publishing 2012), 183.

[9] Schoukens H. and Dotinga H., ‘Natura 2000 and fisheries: A question of competence or willingness?’ in Charles-Hubert Born et al. (eds.), *The Habitats Directive in its EU Environmental Law Context: European Nature’s Best Hope?* (Routledge 2015), 375.

[10] Commission, ‘Guidelines for the establishment of the Natura 2000 network in the marine environment. Application of the Habitats and Birds Directives’ (*European Commission*, May 2007).

[11] Commission, ‘The 2010 assessment of implementing the EU Biodiversity Action Plan’ (Report) COM (2010) 548 final.

[12] European Environment Agency, ‘EU 2010 Biodiversity Baseline’ (*European Environment Agency*, 2010) <http://www.eea.europa.eu/publications/eu-2010-biodiversity-baseline/> accessed 19 April 2016.

[13] Commission, ‘Our life insurance, our natural capital: an EU biodiversity strategy to 2020’ (Communication) COM (2011) 244 final.

[14] Caine C. 2014, The Dogger Bank Offshore Wind Farm Proposal: A Study of the Legal Mechanisms Employed in the Construction of an Offshore Wind Farm, *North East Law Review*, **2**, 92.

[15] 4C Offshore, ‘Project details for London Array’ (*4C Offshore Website*) <http://www.4coffshore.com/windfarms/london-array-united-kingdom-uk14.html> accessed 19 April 2016.

[16] Gosden E., ‘Offshore wind farm scrapped due to fears over birds’ (*The Telegraph*, 19 February 2014) <http://www.telegraph.co.uk/finance/newsbysector/energy/10649631/Offshore-wind-farm-scrapped-due-to-fears-over-birds.html> accessed 19 April 2016.

[17] Harvey F., ‘Migrating birds halt expansion of London Array’ (*The Guardian*, 19 February 2014) <http://www.theguardian.com/environment/2014/feb/19/migrating-birds-london-array-offshore-windfarm> accessed 19 April 2016.

[18] 4C Offshore, ‘Project details for Sikka I-Bajda’ (*4C Offshore Website*) <http://www.4coffshore.com/windfarms/sikka-l-bajda-malta-mt01.html> accessed 19 April 2016.

[19] 4C Offshore, ‘Project details for Cirrus Shell Flat Array’ (*4C Offshore Website*) <http://www.4coffshore.com/windfarms/cirrus-shell-flat-array-united-kingdom-uk24.html> accessed 19 April 2016.

[20] 4C Offshore, ‘NO for Maltese wind farm’ (*4C Offshore Website*, 25 February 2015) <http://www.4coffshore.com/windfarms/no-for-maltese-wind-farm-nid1380.html> accessed 19 April 2016.

[21] Cliquet A. et al., ‘Conflicting Interests between Offshore Wind Farm Development and the Designation of a Natura 2000 Site: riding a Belgian policy roller coaster?’ in von Nordheim and others (eds.), *Progress in Marine Conservation in Europe 2012* (BfN-Skripten 2013), 149.

[22] Qiu W. and Jones p. 2013, The emerging policy landscape for marine spatial planning in Europe, *Marine Policy*, **39**, 182.

[23] Toke D. 2011, The UK offshore wind power programme: A sea-change in UK energy policy? *Energy Policy*, **39**, 532.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas

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[24] Douvere F., 'Marine Spatial Planning: concepts, current practice and linkages to other management approaches' (PhD thesis, Ghent University 2010), Part I, p. 4 <http://www.unescoiocmarinesp. be/uploads /documenten bank/f65e104ce9fcc7ec74f6eda0167d57d9.pdf> accessed 19 April 2016.
[25] Frazão Santos C. et al. 2014, How sustainable is sustainable marine spatial planning? Part I – Linking the concepts, *Marine Policy*, **59**, 62.
[26] Directive 2014/89/EU of the European Parliament and of the Council of 23 July 2014 establishing a framework for maritime spatial planning [2014] OJ L 257 (Maritime Spatial Planning Directive).
[27] Kyriazi Z. et al. 2013, The integration of nature conservation into the marine spatial planning process, *Marine Policy*, **38**, 136-138.
[28] Katsanevakis S. et al. 2011, Ecosystem-based marine spatial management: Review of concepts, policies, tools, and critical issues, *Ocean* and *Coastal Management*, **54,** 817.
[29] Stookes P., 'The Habitats Directive: Nature and Law' in Gregory Jones (ed.), *The Habitats Directive: A Developer's Obstacle Course?* (Hart Publishing 2012), 140.

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Cultural and Social Issues

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Views, needs, attitudes, personal reflections on behavior and demographics of cyclists and affected residents in the city of Preveza, Greece

P. Karanikola[1], T. Panagopoulos[2*], S. Tampakis[1], A. Kontou-Bouglali[1]

[1]Department of Forestry and Management of the Environment and Natural Resources,
Democritus University of Thrace, 193 Pantazidou street, Orestiada, Greece.
[2]Research Center for Spatial and Organizational Dynamics (CIEO), University of Algarve, Gambelas Campus, 8000 Faro, Portugal
*Corresponding author: Email: tpanago@ualg.pt

Abstract

Cycling as a mode of transport is a low-cost, health-improving way to travel and with environmental benefits for the cities that promote it. Only recently, with concerns over climate change and obesity, cities throughout the world are implementing policies to promote cycling, however, in Greece the use of bicycle is limited. In Preveza, a City in Northwestern Greece, where bicycle has a prominence assignment comparatively to other Greek cities, there are efforts to promote cycling by constructing an extensive network of bicycling facilities, implementing transit integration and organizing exhibitions and weekly races for cyclists. This study recorded the views of residents of the city of Preveza about the use of bicycle as a mean of transportation. Through the aid of a structured questionnaire the residents evaluate the suitability of the city for cycling, the existing infrastructure and appropriate education and behavior bicyclists and other drivers. Despite the fact that the majority of the residents have a positive opinion about the bicycle use and they know how to ride a bicycle, the percentage of the unhappy residents cannot be entirely ignored. More than half of residents use the bicycle for their transportation and state that bicycle is a cheap way of transport in the city. Though two third of the residents evaluate the cycling facilities of their city as adequate and unsafe for the young cyclists, which do not follow the code rules of transport. The adult cyclists on the contrary are more loyal to the code but state that the drivers do not respect their presence in the roads.

Keywords: cycling infrastructure; residents' views; cyclists' behavior; transportation

1. INTRODUCTION

The transportation sector is responsible for one third of the CO_2 emissions with motor vehicles to be the main contributor of atmospheric pollution in the word [1]. Short trips with cars contribute disproportionately to emissions because of cold starts [2]. In Europe about 30% of trips with cars cover distances less than 3 km and 50% less than 50 km [3]. A good opportunity for curbing the use of cars is the mode shift from automobile trips using to other transportation forms, called 'active transportation' [4]. The most common forms of active transportation are walking and bicycling.
According to Dekoster and Scollaert [5] 73% of the Europeans think that bicycles should benefit from preferential treatment compare with cars. Interest in the bicycle is on the rise and many towns and cities are pursuing policies to promote its usage is increasing [6, 7].

For cycling, trip distance appears to play a key role [8] because distance is one of the variables that make sometimes the use of bicycle prohibitive for long distance travel and attractive for shorter routes [9].

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In the last two decades, bicycle has become a symbol of sustainable urban transportation, [10,11] with many advantages for cyclists, the society and especially for the environment [12,13]. It is a cheap mode of transportation with low maintenance costs [14], very flexible and relatively fast, it helps to reduce urban traffic congestion levels [15, 16, 3, 17, 18]. Thanks to all these advantages it comes as no surprise that the bicycle has come to be seen as a lifestyle choice[19] that should be encouraged in order to reduce the number of negative marginal effects involved in the usage of private automobiles [16]

Although, it has been observed a lot of interest on promoting bicycling, especially in Canada and U.S, [4, 9, 13, 20, 21]. However, bicycling is underused as a transportation mean in these countries, concerning approximately 1-3% of the trips [6]. In some European countries as Denmark, Germany, Finland, Sweden and Netherlands this percentage is estimated as 10 to 27% [1, 8, 11, 22, 23, 24].

Unfortunately, in Greece cycling used to be a common mean of transport until the 1970's whereas, the lack of safety standards have forced many people to use cars instead regarding their daily transportation needs. During the last years has been an effort to introduce cycling again in the life of people living in cities [10, 11].

The first cycle networks in Greek cities have already been implemented, after a long period of delays in comparison to other European countries [25]. Most of the studies exploring the intention of Greek residents to cycling are focusing in three big cities of Athens, Patras and Volos [8, 26, 27] and there is only one [24] that records resident's attitudes on advantages and disadvantages of cycling in Orestiada (a small size city without cycling net). Because bicycle is quite popular in small and medium size cities around the world [28] the present paper attempt to record the views of residents in a medium city with cycling net. Aim of this study was to explore the needs, attitudes and personal reflections on behaviour and demographics of cyclists and affected residents in the city of Preveza, Greece, and to record resident's views regarding the use of bicycle and their evaluation about existent infrastructure.

2. MATERIALS AND METHODS

2.1. Study Area

Preveza is a town in the region of Epirus, northwestern Greece, located at the mouth of the Ambracian Gulf. It is the capital of the regional unit of Preveza, which is part of the region of Epirus.

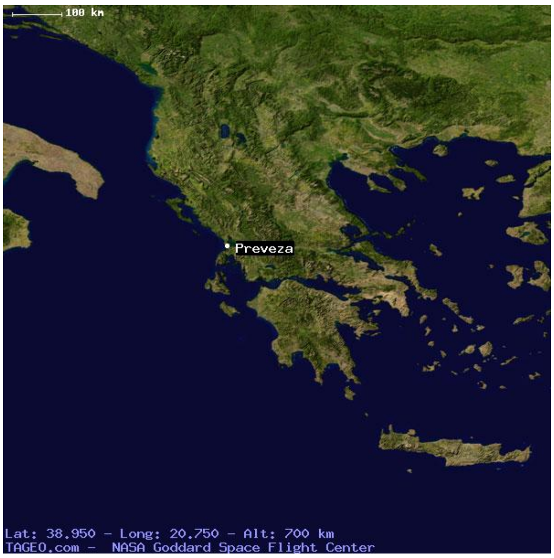


Figure 1. Map of Greece depicting the investigation area

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The data used in this study was gathered at the municipality of Preveza, which is located in northwestern Greece. It is the capital of the regional unit of Preveza, which is part of the region of Epirus with 22,853 residents in 2011 showed a rapid population increase by 13.7% in the last decade [28].

2.2 Research Methodology

The research was carried out with an application of a face to face structured questionnaire. The research area of this paper was the city of Preveza. The sampling method used was simple random sampling [29, 30]

Data were collected in 2013. The population's proportion which is also the objective estimation of the real population proportion p as well as the estimation of the typical error of the population sp, without the correction of the finite population (because the size of the sample is small), was carried out through the use of the formulas of simple random sampling. In order to calculate the size of the sample we carried out pre-sampling, with the size of the sample being 50 individuals. The size of the sample was estimated according to the formulas of simple random sampling (where t = 1.96 and e = 5%) [31] The total number of interviews was 400.

3. RESULTS AND DISCUSSION

3.1 Demographic profile of the respondents

During the interviews, the residents were initially asked about their demographic profile. As shown in Table 1, 46% of the respondents questioned were male and 54% were female. Most of them (33.5%) were young (18-30 years), unmarried (47.2%) and without children (51.8%). As regards their profession, they were mainly self-employees (22%). or public servants (20.8%) Their educational level was quite high, since over 29.8% of the respondents had completed upper secondary school or technological education (22.2%).

Table 1. Socio-demographic profile of the sample %

Gender	Male 46%	Female 54%			
Age	18-30 33.5%	31-40 23.5%	41-50 23%	> 50 20%	
Marital Status	unmarried 47.2%	Married 42.2%	divorced or widowed 10.5%		
Childhood	without children 51.8%	one child 13.5%	two children 24.5%	three children 7.5%	more than three 2.7%
Educational Level	Primary School 3.5%	Lower Secondary 6.8%	Technical School 8.2%		
	Upper Secondary 29.8%	Technological ed. 22.2%	University 29.5%		
Profession	private employee 18.5%	public servants 20.8%	self-employed 22%	farmers or livestock farmers 2.2%	
	pensioners 5.8%	Students 11.5%	housewives 3%	Unemployed 13.8%	
Annual income	≤ 5.000 € 14.2%	5.001 - 10.000 € 14.2%	10.001 - 15.000 € 15%		
	15.001 - 20.000 € 7%	> 20.000 € 6.8%			

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3.2 The bicycle use in the city of Preveza

The city of Preveza is one of the Greek cities with bicycle net near the automobile road for over ten years (Figure 2). At the first part of the questionnaire the residents were asked about their attitudes for the usage of bicycle. According to the results the vast majority of the residents can ride bicycle. Almost all of them (90.5%) are positive to the usage of bicycle and 28.2% use it always, 26% often or sometimes (17.2%) for their mobility needs. Only 1% had negative association to the usage of bicycle with 17.2% never and 11.2% rarely use it, while 8.5% were indifferent.



Figure 2. The bicycle net of Preveza

Comparing the results on a similar research in the city of Orestiada where there isn't bicycle net, the views are completely different. The majority of residents (56.3%) never use bicycle for their transportation and 22% rarely. Only 16.8% use often bicycle and 5% always [23].

Bicyclists to various countries prefer moving in bicycle lanes and paths with moderate elevation in beautiful green landscapes without pollution and noise [33, 34]. The city of Preveza is combining this kind of bicycle network a part of that near the sea (in Amvrakikos gulf one of the most famous biotope in Greece). As regards 45.5% of the residents are of the opinion that the city of Preveza is absolutely suitable to bicycling for their transportation and 19.2% very suitable. Moderate, little or not at all characterized it 23%, 10% and 2.2% respectively. Many studies have shown that cycling infrastructure is, indeed, a necessary prerequisite for the expansion of bicycle use [36].

While the bicycle is quite popular in medium sized cities around the world [27], a recent survey in one Greek city (Volos) found that although Greeks express a high intention to use the bicycle for their daily activities it is also clear that due to the lack of infrastructure residents' are very reluctant to manifest this intention [25].

In the present study the residents of Preveza were asked to evaluate the existing bicycling infrastructure. Most of them evaluated as bad (40.5%) and very bad (18.8%) and 32% as mediocre. Only 7% and 1.8% found the infrastructure as good and very good respectively.

The lack of infrastructure is associated with the lack of safety especially for the children [34]. Safety in the use of bicycle especially for the children seems to bother the residents of Preveza. Almost the half (42.2%) found bicycling as little safe, while 24.2% say that it isn't safe at all. 23% they are indifferent to that attitude and only 7% and 3.5% respectively are of the opinion that bicycle is very or absolutely safe.

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Besides residents of Preveza are of the opinion that young cyclists rarely (43%), never (12%), or sometimes (32.8%) follow the transportation rules of road code. Less residents stated that young cyclists often (11.8%) and always (0.5%) follow the code in their transportation bicycling.
The residents' attitude about car driver's behavior against cyclists is rarely frustrated to 40%, never to 13.2% and 34.8% state that sometimes drivers respect bicyclists on the road. Only 10% consider that happens often and 2% always. Similarly the residents said that most bicyclists don't follow the road code (sometimes 39.8% and rarely 29.2% or never 7.8%). Only about one third of them follow the code (20.5% often and 2.8% always). According to Vlastos et al. [24], in the city of Patras all cyclists (regular and occasional) have the intention to drive without following the road code.
With regard to the question on whether the education and training tests for the young bicyclists has to be instituted, six to ten residents (59.2%) replied positively and 40.8% negatively. In similar research to the city of Orestiada half of them agree with that attitude [23].

The use or not of bicycle is related with the residents' behavior to their natural and social environment regarding their daily transportation [1]. Regarding the question on how the usage of bicycle of other residents can affect to their own decision to use it, 72.5% was positive and 27.5% negative.

3.3. Distance of the trip to use bicycle

Accordig to Dekoster and Scollaert 30% of the trips in the car cover distances of less than 3km [6]. For cycling trip distance appears to play a key role [8]. Regarding the question on the lower distance is need for the use of car or motor bike most residents stated distances more than 3km, while 27.8% of the residents stated distance more than 1.5 km and 37.2% of them for more than 2km (Table 2).

Table 2. What is the lower distance to use car or motor bike?

Distance	Percent	Cumulative percent
always	16.5%	16.5%
100 m	0.2%	16.8%
300 m	0.2%	17.0%
500 m	1.2%	18.2%
1 Km	4.8%	23.0%
1,5 Km	4.8%	27.8%
2 Km	9.5%	37.2%
3 Km	13.0%	50.2%
4 Km	9.5%	59.8%
5 Km	40.2%	100.0%

Bicycle is a very cheap mode of transportation with low maintenance costs [14]. The benefits of investments in cycling infrastructure estimated 4–5 times greater than the costs and concluded that such investments are more beneficial to society than automobile-related transport investments [21]. The residents of Preveza had also of the same opinion. A great majority of them characterize bicycling as very cheap (40.8%) or cheap (36.2%), with few found it very expensive (1.8%) and expensive (4%) and 17.2% were of the opinion that cycling is either expensive or cheap mode of transportation.

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4. CONCLUSIONS -PROPOSALS

The city of Preveza is one of the Greek cities that bicycle is popular mode of transportation. The results of the present study showed that the vast majority of the residents can ride bicycle and they have positive view for bicycle. More than half of them use it always or often for their daily transportation. On the contrary the residents of Orestiada [23] never of rarely use bicycle. These results were similar to that found for all Greek cities according to Dekoster and Scollaert [6], where 7.5% of the residents are regular and only 1.8% occasional cyclists. Thus, it can be concluded that the usage of bicycle in Preveza is more like Danish cyclists with 50.1% regular cyclists and 8% occasional.

Preveza is a city with moderate elevation and beautiful green landscapes suitable or very suitable for cycling according to the majority of the residents. Although, they evaluate the existing infrastructure as bad or very bad. This lack of infrastructure is associated with less safety especially for children [36]. The residents found the use of bicycling little of not at all safe especially for the children because especially young cyclists only rarely or sometimes follow the high way code. Besides, most of the drivers do not respect cyclists on the road. A good way to change the current situation is to consecrate the training tests to young cyclists.

The usage of bicycles from other residents affect positive to their own decision to use it. And because distances play an important role to use cars or bikes [8] most of the residents state that distance more 2km is deterrent to the use of bicycle.

There are many ways that bicycle usage can be encouraged, including the building of an extensive bicycle network. Another proposal is the possibility is to develop a public network of single-use hire bicycle stations for one-way trips. This policy has good results in recent years to many European countries thanks to the development of smart bicycles [23] which have reduced the threat of theft and vandalism, which are two of the greatest risks to bicycle usage development.

References

[1] Aldred, R., 2010. On the outside: constructing cycling citizenship. *Social and Cultural Geography*, **11(1)**, 35-52.

[2] Unger, N., Bond, C., Wang, S., Koch, M., Menon, S., Shindell, T. and Bauer, S., 2010. Attribution of climatic forcing to economic sectors. *Proccedings of the National Academy of Science*, **107**, 3382-3387.

[3] Nazelle, A., Morton, B., Jerrett, M. and Crawford-Brown, D. (2010). Short trips: An opportunity for reducing mobile-source emissions*? Transportation Research Part D*, **15**, 451-457.

[4] Teschke, K., Brubacher, J., Friedman, S., Cripton, P., Harris, A., Reynolds, C., Shen, H., Monro, M., Hunte, G., Chipman, M., Cusimano, M., Smith Lea, N., Babul S., and Winters, M., 2012. Personal and trip characteristics associated with safety equipment use by injured adult bicyclists: a cross-sectional study, BMC *Public Health*, **12,** 765.

[5] Lumb, P. (2012). Cycling, walking and biodiversity: occupying urban landscapes. Proceedings of the Fourth Austalian Cycling Conference 16-17 January, pp. 107-119.

[6] Dekoster, J., Scollaert, U., 1999. Cycling: The way ahead for towns and cities. European Commission, Luxemburg.

[7] Martens, K., 2007. Promoting bike and ride: the Dutch experience. *Transportation Research* A, **41 (4),** 326–338.

[8] Milakis, D., 2015.Will Greeks Cycle? Exploring Intention and Attitudes in the Case of the New Bicycle Network of Patras. *International Journal of Sustainable Trasportation* **9,** *321-334.*

[9] Guinn, M.J., Stangl, P., 2014. Pedestrian and bicyclist motivation: an assessment of influences on pedestrians' and bicyclists' mode choice in Mt. Pleasant, Vancouver. *Urban, Planning and Transport Research: An Open Access Journal*, **2(1)**, 105–125.

[10] Milani Medeiros, R. Duarte, F., 2014. Policy to promote bicycle use or bicycle to promote politicians? Bicycles in the imagery of urban mobility in Brazil. *Urban, Planning and Transport Research*, **1(1),** 28–39.

[11] Sick Nielsen A.T., Skov-Petersen H., Carstensen, A.T. 2013. Urban planning practices for bikeable cities – the case of Copenhagen. *Urban Research & Practice*: **6**, 110-115.

[12] Chapman, L., 2007. Transport and climate change: a review. *Journal of Transport Geography*, **15 (5),** 354–367.

ISBN: 978-960-6865-94-7

[13] Handy, S., Van Wee, B., Kroesen, M., 2014. Promoting Cycling for transport: Research Needs and Challenges. *Transport Reviews*, **34,** 4-24.
[14] Horton, D., 2006. Environmentalism and the bicycle. *Environmental Politics*, **15**, 41–58.
[15] Hopkinson, P. and Wardman, M., 1996. Evaluating the demand for new cycle facilities. *Transport Policy***, 3,** 241–249.
[16] Castillo-Manzano I.J., Sanchez-Braza, A., 2013. Can anyone hate the bicycle? The hunt for an optimal local transportation policy to encourage bicycle usage transportation policy to encourage bicycle usage. Environmental Politics, 22(6), 1010– 1028.
[17] Tight, M., Timms, P., Banister, D., Bowmaker, J., Copas, J., Day, A. 2011. Visions for a walking and cycling focused urban transport system. *Journal of Transport Geography,* **19(6),** 1580-1589.
[18] Jappinen, S., Toivonen, T., Salonen, M., 2013. Modelling the potential effect of shared bicycles on public transport travel times in Greater Elsinki: An open data approach. Applied Geography, 43, 13-24.
[19] Horton, D., 2007. Fear of cycling. In: D. Horton, P. Rosen and P. Cox, eds. *Cycling and society*. Aldershot: Ashgate Publishing Ltd, 133–152.
[20] Su, J., Winters, M., Nunes, M., Brauer, M., (2010).Designing a route planner to facilitate and promote cycling in Metro Vancouver, Canada. *Transportation Research Part A* **44**: 495–505
[21] Pucher, J. and Buehler, R., 2005. Cycling trends and policies in Canadian cities. World Transport Policy and Practice, 11 (1), 43–61.
[22] Pucher, J., Buehler, R., 2008. Making Cycling Irresistible: Lessons from The Netherlands, Denmark and Germany. Transport Reviews, 28 (4), 495–528.
[23] Tampakis, S., Karanikola, P., Tsantopoulos, G., Andrea, V., Antipa, N.M., Paroni, D.V., 2013. Exploring the positive and negative impacts of bicycling in the city of Orestiada, Greece. *Virtual International Conference on Advanced Research in Scientific Areas* (ARSA-2013) Slovakia, 2 - 6 December 2013, 346-350.
[24] Vlastos, T., Milakis, D., Athanasopoulos, A., 2005. The Research for Cycling in Greece. Methodology of Planning, Infrastructure Standards and a Typology of Design Solutions. *15th International Velo-City Conference*, Dublin, 31 May - 3 June 2005.
[25] Papavasileiou, C., Milakis, D., Vlastos T., 2010. Car dependence or appetence? Examination of attitudes towards sustainable mobility in the Greek case. *Proceedings of the 12th World Conference on Transport. Research*, Lisbon, Portugal, July 2010.
[26] Vlastos T., Milakis, D., 2003. Planning of a cycling network in a Greek city according to geometrical criteria. The case of Moschato", *Tech. Chron. Science Journal*, TCG, I, 2003, (**1-2),** 35-46.
[27] Milakis D., Athanasopoulos, K., 2014. What about people in cycle network planning? Applying participative multicriteria GIS analysis in the case of the Athens metropolitan cycle network. *Journal of Transport Geography*, **35**,120-129.
[28] Hellenic Statistical Authority 2011. http://www.statistics.gr/portal/page/portal/ESYE/BUCKET/General/resident_population_census2011rev.xls (Accessed 1-2-2016).
[29] Meyerhoff, J., Liebe, U., Hartje, V., 2009. Benefits of biodiversity enhancement of nature-oriented silviculture: Evidence from two choice experiments in Germany. *Journal of Forest Economics*, **15**, 37–58.
[30] Hoyos, D., 2010. The state of the art of environmental valuation with discrete choice experiments. *Ecological Economics*, **69**, 1595–1603.
[31] Pagano M., Gauvreau, K., 2000. Elements of Biostatistics. Ellin Publications, Athens.
[32] Winters, M., Davidson, G., Pearce, C., Teschke, K., 2007. Cycling in Cities – Understanding people, neighbourhoods and infrastructure to guide urban design for active transportation. *45th International Making Cities Livable Conference*, Portland, OR, June 10-14, 2007.
[33] Winters, M. Brauer, M., Setto E.M., Teschke, K., 2013. Mapping bike ability: a spatial tool to support sustainable travel, *Environment and Planning B: Planning and Design*, **40(5)**, 865- 883.
[34] Pucher, J., Buehler R., Seinen, M., 2011. Bicycling renaissance in North America? An update and reappraisal of cycling trends and policies. *Transport Research Part A*, **45**, 451-475.
[35] Buehler, R., Pucher, J., 2012. Cycling to work in 90 large American cities: new evidence on the role of bike paths and lanes. *Transportation*, **39**, 409–432.
[36] Reynolds, C., Winters, M., Ries, F. and Gouge, B. 2010. Active Transportation in Urban Areas: Exploring Health Benefits and Risks. *Evidence review*, June 2010.

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Sustainable Architecture, Planning and Development

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Proposal for a historic-cultural accessible route in the Historic Centre of Faro city as an opportunity for sustainable urban planning

S. Silva Costa, T. Panagopoulos*

Research Center for Spatial and Organizational Dynamics (CIEO), University of Algarve,
Gambelas Campus, 8000 Faro, Portugal
*Corresponding author: Email: tpanago@ualg.pt

Abstract

Europe's historical cities are renowned worldwide for their beauty, diversity and historical significance. Millions of people visit them every year but many others do not have this opportunity due to physical barriers and inadequate services that can prevent people with sensory or physical disabilities from accessing them. Current tendencies worldwide indicate that culture and tourism will play a significant role in the future of the European cities. Although trends differ between countries, populations of nearly all developed countries are ageing, which will increase the challenges of disability rates in elderly people and therefore will have a fundamental effect on sustainability of modern society. Local governments must acquire new knowledge to manage diverse and multicultural cities with ageing population. This study proposes a technical, formal and aesthetic solution that respect the spirit of place and is integrated at the Plans of Accessibility and Pedestrian Mobility of the city or region. It proposes solutions to discipline traffic and car parking, its coexistence with pedestrian, traffic calming measures, exclusively pedestrian streets, removal of architectural and urban barriers, improvement in public transport offer and promotion of multifunctional spaces. The proposal for a historic-cultural accessible route in the historic centre Vila Adentro is an opportunity for Faro sustainable planning, contributing to the affirmation of its centrality and an opportunity for rehabilitation of public spaces, improving their accessibility and mobility, making it more appealing and inviting, attracting and generating the most varied kind of experiences and opposing the abandonment process and degradation that had suffered in recent decades.

Keywords: accessibility and mobility; historic city center; ageing; urban planning

1. INTRODUCTION

The historic centres have suffered different pressures with urban sprawl which has been verified in recent decades, resulting in the abandonment and consequent degradation of some of its public spaces and buildings. After years of degradation, the historical areas aroused in the interest of the population in general, and especially because of the tourism potential. This new paradigm took place mainly by the fact that these areas are considered 'the most representative pieces of the urban fabric and constitute a symbolic space that identify, distinguish and give identity to the cities' [1]. One of the main conflicts typical of already consolidated urban areas is the lack of accessibility, enhanced by problems such as road traffic in narrow roads unsuitable for the use of private car, the characteristics of the road network and urban morphology (narrow streets and shortage of public space) [2]. The resolution of these problems is the key to the rehabilitation of these central areas.

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The perspectives of exclusion of mobility are enormous challenges to the future planning of cities, taking into account that the city should be designed including the concepts of accessibility and urban mobility, discarding the idea of elimination of a simple barrier, giving rise to a system of continuity [3,4]. However, particular sections of society such as the ageing population, the disabled and minority groups may not have the same opportunities and access the old city centers that more affluent sections of society enjoy. To understand why, researchers have turned to the perspective of environmental justice [5]. 'Social justice refers to the principles, values and belief that every individual and group is entitled to fair and equal treatment, which is necessary for the achievement of a society in which all people have equal access to rights, not only under law, but in all aspects of life, and all people get an impartial share of the benefits as well as carry a fair share of the responsibilities of society' [6,4].

The "imobilitys" that draw the urban territories constitute a problem for the sustainable development of cities, and it is urgent that the accessibility and mobility for all is a factor to be taken into account in the planning, development and management in different scales (national, regional and local) [7]. So, a historic centre integrated in a city with a balanced mobility, connected by an accessible pedestrian network, allows to oppose the current patterns of urban growth dispersed based on the vehicle domain. It is in this sense that the concern facing the issues of accessibility and mobility in historical areas, has gained some relevance within the urban planning, contributing to the readability of public space and for the enhancement of the existing heritage.

Objective of this study is to propose a technical, formal and aesthetic solution that respect the spirit of place, opposes the abandonment process and degradation that had suffered in recent decades and is integrated at the Plans of Accessibility and Pedestrian Mobility of the city of Faro, Portugal.

2. MATERIALS AND METHODS

2.1 Study area

The historical centre is the heart of the city of Faro and coincides with the city's oldest urban area, which is made up of three historical nuclei: the Vila Adentro, the Mouraria and the Bairro Ribeirinho. The study area is confined to the perimeter of the Vila Adentro and its surroundings (figure 1). The Vila Adentro assumes, in the context of the city, a historical-cultural significance beyond question, for its organized built form and set elements that remain intact in the face of requests that threaten the rest of the city [8]. It has an environment of exception, due to the nature of public space and the quality of buildings (including two of the three buildings in the municipality, classified as national monuments) and is still the area with greater definition of its boundaries, due to walled belt. This historical nuclei strengthens its uniqueness by direct contact with the Natural Park of Ria Formosa (wetlands).

2.1 Collection and analysis of information

This step helped clarify concepts and aspects that serve as a basis for understanding and theoretical framework of the proposal. The collection of information was supported in research and interpretation of bibliographic and iconographic sources about: accessibility and mobility in historical centres; its importance and its absence as one of the main factors which contribute to their degradation/abandonment; the problems in these situations as well as solutions and strategies of urban rehabilitation, urban regeneration.

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Figure 1. Delimitation of the study area Vila Adentro (background from Google Earth).

2.2 Characterization of the study area

A characterization of the area of study was done analyzing different materials and existing realities in the study area. Bibliographical interpretation about its genesis and evolution and background or studies already carried out; visits/fieldwork; photographic survey of existing situations; inventory of the types of problems/barriers identified; production of schematic drawn pieces (in different scales) assisted in the interpretation of the conclusions about analysis and characterization. The spatial configuration was one of most important schematic drawings because provided useful information about the best routes and streets in the old city to reach to public space from the point of view of quality in the accessibility [9].

Through the adopted methodology it was possible to identify and raise questions related to their current situation, including its biophysical and cultural characterization, their potential/opportunities and problems/risks. And through the collected elements have been possible a synthesis of the analysis and characterization of the study area and the development of a SWOT analysis (Table 1) which brings together all relevant aspects.

2.3 Proposal

The proposal was developed at the level of the conceptual Master plan and represented through drawn pieces, which reflect all aspects collected and analyzed in a design drawing. Some of the proposals that were already approved by the City Council were also considered. The proposal was also supported by a concept and strategy(s), which, along with the analysis and characterization of space, justify the choices made.

At this stage it was necessary to approach the area of intervention in two different scales, a first that represented the proposal in its entirety and a second that represented different areas of intervention thus allowing phase the proposal according to its priority.

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Table1. SWOT analysis of the study area

Internal factors	
Strengths	**Weaknesses**
-Central geographic location; -Intramural Area with free access to the pedestrian; -Monumental character and Strong asset value; -Urban Structure that provides some urban public spaces (squares) with considerable dimensions for the realization of activity and events; -Existence of cultural equipment; -Existence of archaeological remains (e.g. Roman Forum in Largo da Sé) -Environmental Quality without visible degradation; -Landscape with excellent panoramic views to the Ria Formosa and to the docks; -Appearance of small restaurants with quality; -Existence of public parks and a linear garden near the walls, which contribute to the drainage and water infiltration in the intramural area; -Proximity to main hotel equipment; -Proximity to major stations of collective transport;	-Decline and ageing of the population; -Inability to investment on the part of the residents; -Preference in public and religious services installation; -Absence of equipment to support residents and users; -Degradation of some buildings and pavements in public space; -Squares and streets dominated by traffic and car parking – gives rise to conflicts and discourages pedestrian circulation; -Rudimentary green structure – absence of vegetation in the streets; -Night insecurity; -Physical barrier caused by railroad, which breaks the physical links between the city and the Ria Formosa;
External factors	
Opportunities	**Threats**
-Initiatives to revitalize the monumental character and heritage value; -Buildings and spaces available for new uses; -Benefits and tax breaks to owners;	-Economic crisis and reduced ability of public and private investment; -Large area of archaeological sensitivity; -Tendency of depopulation and population ageing; -Proximity to the railroad;

3. RESULTS AND DISCUSSION

3.1 Programme and concept

The intervention was carried out in spaces already consolidated, so the program was previously set and the proposal gave response to the accessibility and mobility problems identified and to obstacles of recreational and leisure functions spaces provide. Formalizing in a Master plan, some of the intentions and existing functions, such as the walking routes, road routes and parking areas, rest areas, multifunctional spaces for events and activities and designing the path for bikes and pedestrian, was another of the purposes of this proposal. However this proposal respects the multifunctionality that characterize the study area, which allows easy adaptability to different realities. This way it was avoided a design directed specifically to a single function and consequently it was minimized the possibility of these spaces become uninteresting or obsolete.

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The concept that structure the proposal consists of a Historical-Cultural Accessible Route, which connects all the spaces and buildings of interest, having as reference 4 main points of access to the Vila Adentro, the 4 Doors: Arco da Vila, Porta Nova, Porta do Castelo and Arco do Repouso. The name of the route is known as the Route of the 4 doors and is represented in figure 2.

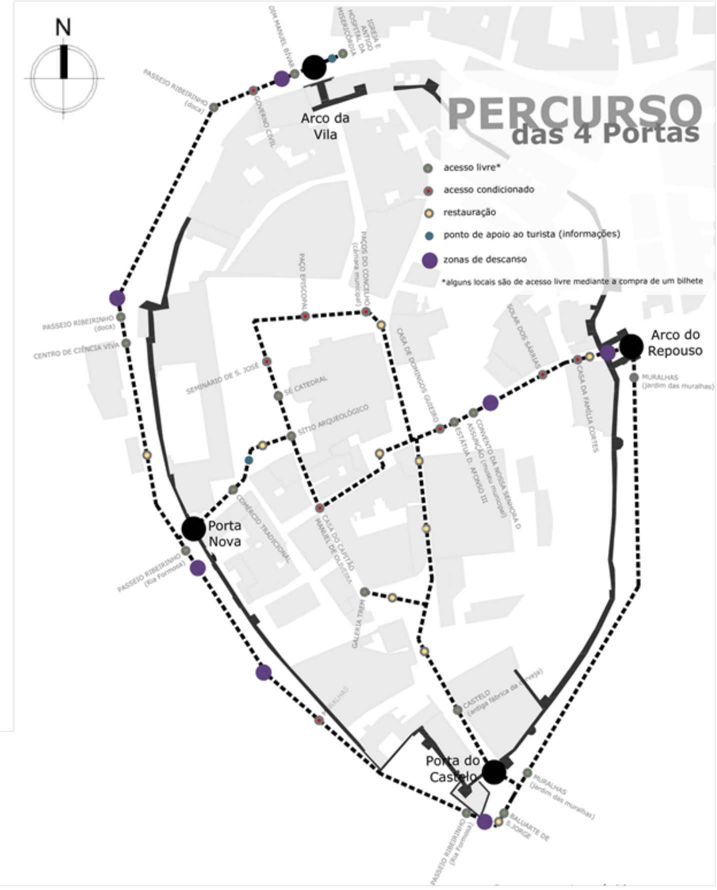


Figure 2. Route of the 4 Doors, schematic drawing of the intervention concept.

3.2 Strategies

The strategies that support the Route of the 4 Doors and structure the proposal consist of:

- Increase the area allocated to soft modes: optimization of pedestrian flows through the creation of an accessible route, reducing the area devoted to motor traffic, increasing and formalization of the bike path and walking routes – in order to comply with the ground level of buildings;
- Functional restructuring of small squares and open public space, through the design of pedestrian areas and allocation of urban furniture to support activities;
- Enhancing city resilience to climate change by means of ecosystem services improvement with the increase of permeable areas and thermal comfort through the introduction of autochthonous vegetation and permeable materials, taking into account the criteria of the space, the historical-cultural urban character and the comfort of its users [8];
- Organization of the infrastructure and street furniture to enhance environmental quality and human well-being [10];

With those strategies it was enviosioned to make the historic centre aproachable to the citizens.

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3.3 Proposal of intervention

The proposal of the Historical-Cultural Accessible Route is parallel to the whole area of intervention and considers an organization of road flows and pedestrian flows [11]. This new route was only considered where it would not damage significant fabric or character of Vila Adentro and a few management solutions was able to eliminate or reduce the need for great physical interventions [12].

The accessible route of the 4 Doors is equipped by informational boards with the same design of plates proposed by the City Council, for placement in buildings classified as historical (figure 3).



Figure 3. Example of informational plate for the Route of the 4 doors.

The Porta Nova is one of the most strategic access to the intramural area due to its proximity to the boat boarding point. As such, and due to the conflicts car versus pedestrian and the large number of architectural and urban barriers, it was proposed to put this whole area at the same height of the existing rides. The link to the Largo da Sé, made through the Porta Nova Street, was established through a pedestrian accessible channel with 1.50 m wide, in limestone slabs (figure 4). The pedestrian accessible channel is a proposal used in every street of Vila Adentro with these features, this way all the constructive elements and their visual integrity were preserved, ensuring at the same time the pedestrian accessibility.



Figure 4. Before and after the proposal of intervention at the Porta Nova Street.

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Repairing degraded pavements was another proposal to the whole intervention area, maintaining the integrity of the built heritage and preserving the existing permeable areas [13,14]. Example of this case is the linear Garden of Walls, where after the intervention was guaranteed a corridor with accessible semipermeable or permeable materials (e.g. porous concrete), that respect the environment provided by walls (figure 5).



Figure 5. Before and after the proposal of intervention at the Garden of Walls, near the São Francisco square.

In the most sensitive areas to the level of conflict between the automobile and pedestrian areas were proposed areas with the same height in all of its extension, avoiding gaps created by curbs and providing the priority of the pedestrian over the car [15]. In figure 6 can be seen an example of this proposal for the main accesses to the Vila Adentro at the Arco do Repouso.



Figure 6. Before and after the proposal of intervention at the Arco do Repouso.

In relation to vegetation and thermal comfort of the public space, the biggest challenge focused on the Riverside Walk of Faro, which recently due to a plague lost its tree alignment, with tropical origin (Palm Trees). The replacement of the green corridor in this area with great intensity of sunlight in the afternoon was inevitable. This proposal was given preference to the choice of trees of the local flora, well adapted to the region's climate and greater disease resistance capacity. The other squares in the study area have tree alignment (e.g. Citrus Tree) well adapted to the volumes and morphology of the built heritage, as well to the clime. And much of the flow of rain water occurs in the private parts of the building such as patios, gardens and courtyards, which are the 'Green Lung' of the Vila Adentro. In figure 7 these green spots can be seen.

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Figure 7. Aerial photography of Vila Adentro and surroundings. (source: www.rotasturisticas.com)

4. CONCLUSIONS

The streets and squares structure of Vila Adentro allowed very few challenges in terms of readability of public space. Financial constrains requiring a project with not very ambitious proposals was a limitation of the study. However, the greatest challenges on accessibility and mobility, were identified critical areas that were not respecting the current legislation. Also, there was a slight disorganization of the road traffic and parking, which harms the soft modes, but these problems were insignificant compared to other historical centres with the same characteristics. It was found that the architectural and urban barriers were the biggest physical obstacles. These factors combined with the current economic crisis of the country and the shortage of human resources, has allowed to develop simple minimalistic and easy to perform proposal, which somehow facilitates interventions and speeds up the approval process of the work. The fact that the proposals were simple became an opportunity to preserve the existing tracing of urban design, making visible in the new proposals the layers of time in the public space of old town. This way, the heritage of public space and its construction processes were preserved.

It is expected that despite this proposal solve some of the existing problems in the Vila Adentro, there is still much that can and should be done, not only in the old town but also in relation to its links with the rest of the city. The proposal of the Route of the 4 Doors at this preliminary design phase of conceptual design and feasibility study, provides a means and not an end. The following development phase of Master Plan may undergo some changes due to the need for public hearing in a process of public participation. Public participation takes into account the views of users of space, adapting the project to their needs [16], which makes this a very important process for the following stages and will be the aim of future reasearch.

References

[1] Sáez, C. C. 2009. *La Ciudad para el peatón: las ciudades históricas en la movilidad urbana*. Ingeniería y Territorio: movilidad urbana. 86, 58–67.
[2] Puebla, J. G. 1995. *Movilidad, Medio Ambiente y Patrimonio Histórico-Artístico en las Ciudades Históricas*. Anales de Geografía de la Universidad Complutense. 15, 375–381.
[3] Portas, N. 1981. *Velhos centros vida nova*. In Os Tempos das Formas, volume I: A Cidade Feita e Refeita. Guimarães: Universidade do Minho, p. 155–170.
[4] Zanirato, S. H. 2008. *Mobilidade nas Cidades Históricas e a Proteção do Património Cultural*. Revista Eletrónica de Turismo Cultural. 02:02, p. 1–16.
[5] Byrne J., Wolch J., Zhang J. 2009. *Planning for environmental justice in na urban national park*. Journal of Environmental Planning and Mangement, 52, 365-392.

ISBN: 978-960-6865-94-7

[6] United Nations, 2009. *Creating an inclusive society: practical strategies to promote social integration*. Department of Economic and Social Affairs, New York.
[7] Teles, P. 2015. *A Cidade das (I)mobilidades: Manual Técnico de Acessibilidades e Mobilidades para Todos*. Mobilidade e Planeamento do Território, Lisbon.
[8] Berte, E. Panagopoulos, T. 2014. *Enhancing city resilience to climate change by means of ecosystem services improvement: A SWOT analysis for the city of Faro, Portugal*. International Journal of Urban Sustainable Development, 6, 241-253.
[9] Talav Era, R. 2012. *Improving pedestrian accessibility to public space through space syntax analysis. Eight International Space Syntax Symposium*. PUC. Santiago.
[10] Panagopoulos, T., Duque, J.A.G., Dan, M.B. 2016. *Urban planning with respect to environmental quality and human well-being*. Environmental Pollution, 208: 137-144.
[11] CMF. 2011. *Conversão da Área Crítica de Recuperação e Reconversão Urbanística em Área de Reabilitação Urbana* – Vila Adentro do Centro Histórico de Faro. Municipility of Faro, Faro.
[12] Shaffrey Associates Architects and Fionnuala Rogerson Architects. 2011. *Access improving the accessibility of historic buildings and places*. In DONNELLY, Jacqui (Ed.) – Advice Series. Ireland: Government of Ireland.
[13] Kaymaz, I. 2013. *Urban Landscapes and Identity*. In ÖZYAVUZ, Murat (Ed.) - Advances in Landscape Architecture. Turkey: InTech, p. 739–760.
[14] LTNZ, Land Transport New Zealand. 2007. *Pedestrian Planning and Design Guide*. Wellington, New Zealand.
[15] Ribeiro, S.B. 2014. *Mobilidade e Acessibilidade Urbana em Centros Históricos*. IPHAN, Brasília, Brazil.
[16] Ribeiro, G.B., Martins, L.B., Monteiro C.M.G. 2012. *Methodological proceedings to evaluate the physical accessibility in urban historic sites*. 18th World congress on Ergonomics – Designing a sustainable future. Work, 41: supplement 1, 4149-4156.

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Environmental research regarding comfort conditions and microclimate in urban open spaces

P. Kosmopoulos*, K. Michalopoulou

Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements,
Democritus University of Thrace, 67100, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

This study aims at measuring the effect of design parameters of outdoor urban spaces to the microclimate and the comfort conditions, by taking into account each parameter of the microclimate, doing a comparative analysis between them, and drawing conclusions, for five different outdoor urban spaces and in all four seasons. Taking into account the analysis of the design parameters and the effects of design interventions to the microclimate, it focuses on thermal indices expressing the conditions of thermal comfort of pedestrians outdoors.

The survey was conducted in five open spaces in the city of Kastoria, south oriented, which had the same relief, but varied in the coating materials, and therefore the measurement results were comparable.

As part of the survey, a series of field measurements of environmental parameters took place. Specifically measured were the air temperatures, surface temperatures, blackball and wet bulb temperatures, the relative humidity, wind speed and solar radiation, incident and reflected. Measurements were made in all four seasons of the year and in particular the periods: summer 12-17 July, autumn 20-25 October, winter 22-28 December and spring 16-21 April. The aim was to draw conclusions about the impact of materials in the forming of temperatures: surface, air, black ball and wet bulb, and the forming of the surface temperature, relative to the incident and reflected radiation. It should be noted that the field measurements in open spaces, were made with portable instruments and not by automatically recording machines which, as known, operate without the direct control of the researcher, thus ensuring direct control of the results and thoroughness of the measurements. Moreover questioners for the subjective responses have been collected.

In conclusion, it is shown that the replacement of hard materials with perforated materials or grass, greatly improves the thermal comfort conditions, while it appears that the planting of large trees, deciduous with rich top, significantly improves the thermal comfort conditions during the day. The survey results show clearly with numerical data the temperature variation in the open spaces, and over different coating materials, the diversification of thermal conditions in these areas, by linking them with thermal indices during the day, at different time periods. Also noted and documented with field measurement data and the results of simulations, is the negative effect of highly reflective surfaces of the open spaces in thermal comfort conditions, mainly during the effect of solar radiation.

Keywords: comfort conditions; microclimate; open urban spaces.

1. INTRODUCTION

This study attempts to benchmark the effect of design parameters of outdoor urban spaces to the microclimate and the comfort conditions, by taking into account parameters of the microclimate, doing a comparative analysis between them, and drawing conclusions, for five different outdoor

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urban spaces and in all four seasons. It also focuses on thermal indices expressing the conditions of thermal comfort of pedestrians outdoors.

The survey was conducted in five open spaces in the city of Kastoria, south oriented. The spaces selected for the field survey were selected to be approximately in the same area within the urban web, with as similar characteristics as possible in terms of orientation and relief, while the differences focus on the coating materials, the quality and quantity of green, and the use of space. Therefore the measurement results were comparable.

As part of the survey, a series of field measurements of environmental parameters took place. Specifically measured were the air temperatures, surface temperatures, blackball and wet bulb temperatures, the relative humidity, wind speed and solar radiation, incident and reflected. Measurements were made in all four seasons of the year.

The aim was to draw conclusions about the impact of materials in the forming of temperatures: surface, air, ball and wet bulb, and the forming of the surface temperature, relative to the incident and reflected radiation [1]. It should be noted that the field measurements in open spaces, were made with portable instruments and not by automatically recording machines which, as known, operate without the direct control of the researcher.

In order to estimate the thermal comfort conditions in the outdoor areas studied, questionnaires were distributed, which asked users of the open spaces to reply during the summer and winter, to questions about the perceived by them thermal environment, to determine the degree of thermal comfort and to suggest ways to improve comfort conditions in those spaces. Moreover, simulation models were used to study the thermal comfort in the measurement areas, using data from the measurements for all four periods of measurements [2].

As a result, the survey was completed with the combination of the data from the field measurements, the questionnaires and the simulation models. Subsequently, experimental interventions with changes in the coating materials in the subject areas are proposed, through simulations, and the results of the analysis of the effect of these on the microclimate and the thermal conditions in the open spaces are described.

In conclusion, it is shown that the replacement of hard materials with perforated materials or grass, greatly improves the thermal comfort conditions, while it appears that the planting of large trees, deciduous with rich top, significantly improves the thermal comfort conditions during the day.

2. EXPERIMENTAL RESEARCH (THE FIELD STUDY)

The aims of the present study are:

- The research regarding the interrelationship between urban morphology and urban macroclimate
- The study of parameters that affect the urban microclimate
- The study of thermal comfort conditions in relation to morphological and microclimatic aspects (software)
- The analysis of the thermal comfort conditions of the people in urban open spaces
- The comparative study of the design aspects and how they affect the urban microclimate and comfort conditions
- The study of how covering materials affect the urban microclimate

The important data of the paper are the following:

- The experimental research regarding basic parameters on site, of five urban open spaces of different use, and different covering materials and different existence of green (grass and trees)
- The research, evaluation and comparison of the results that have been collected during the four seasons of the year

- On site measurements at urban open spaces, with portable instruments, regarding:
- surface materials temperature, air temperature, black ball temperature, W.B.T., incident and reflected solar radiation, air velocity, and relative humidity
- The evaluation of how the above parameters affect the thermal conditions, and afterwards, how the proposed interventions ameliorate the conditions through the use of appropriate software
- At the same time, evaluation and comparative study of the results that came out of the questionnaires filled in by the users of the specific spaces

Methodology and Measurements of the experimental procedures include:

The research has been carried out in Kastoria city, in northern Greece, during the four seasons of a whole year, covering five central open spaces (squares, parks) of the city. For seven days per winter, spring, summer and autumn, three times a day (morning, noon and afternoon) at five specific points of each place, the following parameters have been investigated: air temperature, relative humidity, air velocity, black ball temperature, and incident and reflected solar radiance on specific materials and surfaces with the appropriate portable measurement. The data gathered have been elaborated by appropriate software in order to come to fruitful conclusions.

Parallel to the measurements, during all phaces, questionnaires regarding the subjective comfort conditions have been collected from the users of the specific spaces, in order to be compared to the measurements. Finally, important conclusions regarding the behavior of the existing materials have been extracted.

3. MEASURMENTS OF THERMAL CONDITIONS (EXAMPLARY)

- On site measurements with portable instruments, at five open spaces, at several different points and covering materials
- Four seasons measurements, (winter, Spring, Summer and Autumn), seven days per season, three times per day (morning, noon and afternoon), at all selected places, at all the specific points by all the instruments (19 points, 25 days, 3 times a day, 8 parameters, 11400 manual measurements at all)
- Comfort conditions have been measured at the height of 1.00 ~ 1.50m from the ground after Kosmopoulos [3] in order to cover conditions of all persons involved (young, old, seated e.t.c.)
- Questionnaires answered by the users of the places
- Analysis and elaboration of the data collected
- Models of the comfort conditions as measured and after the proposals for interventions, by the use of appropriate software
- Final proposals for the five open spaces that have been studied, aiming at better comfort conditions for the people

The study areas of the research are observed in Fig.1. The Dolcho Square, the Olympic Flame Park, the Prefecture Square, the Public market and the Grammou Street are the investigated areas.

The Dolcho Square is an area of 1075m^2. The surrounding buildings are mostly houses of one, two or three storeys and the height is 3, 6 and 9m respectively. The width of the north road is 8m, of the south 6m and of the west 9m.

The Olympic Flame Park occupies an area of about 28.550 m^2. The height of the surrounding buildings is 9, 12 and 15m. The width of the north road is about 12.5m, of the south road is 14.5m and of the west side 12.5 m. The park is covered mainly by grass, while the coating routes (width 3.5m. - 5.5m.) is covered by slate.

The Prefecture Square has SSW orientation, it is adjacent to a lake and its area is about 3130m2. The height of the surrounding buildings is 9, 12 and 15 m. The width of the east street is 12.5 m and of the north street is 14.5m. The square is coated by asphalt and there are rows of trees in order to create shadowing conditions to parked cars.

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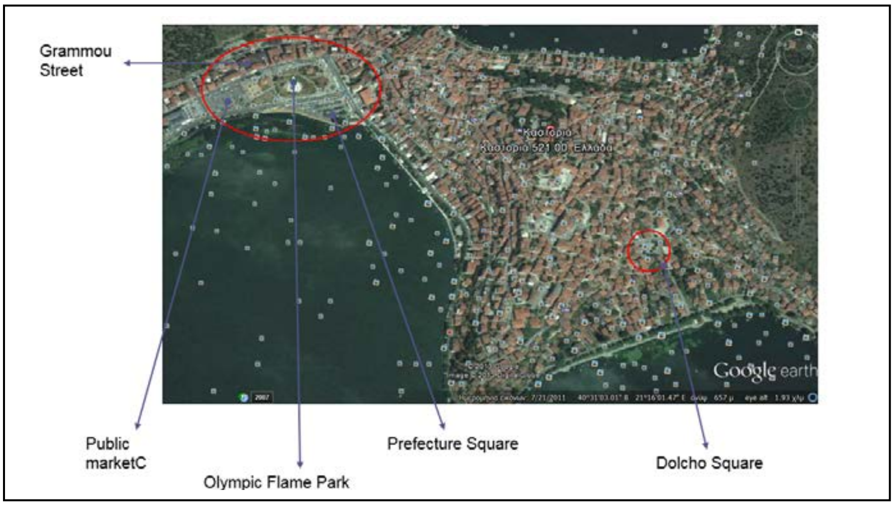


Figure 1: The study area

The parking of the market square occupies an area of approximately 6161m^2. The buildings which are located on the north side have 9, 12 or 15m height. The width of the north street is about 6.5m, of the south is14.5m, of the west 8.5m and of the east street is 6.5m.
The Grammou Street has W-E orientation and it is covered by asphalt. The pavements in each side of the road is 1.5m width and they are covered by white plates. The buildings on each side of the road is 3-5 stories and the average height of the buildings is 12-15m. The width of the road is about 8 meters, and the ratio H/W=1.87. This ratio has as a consequence the downgrading of comfort conditions.

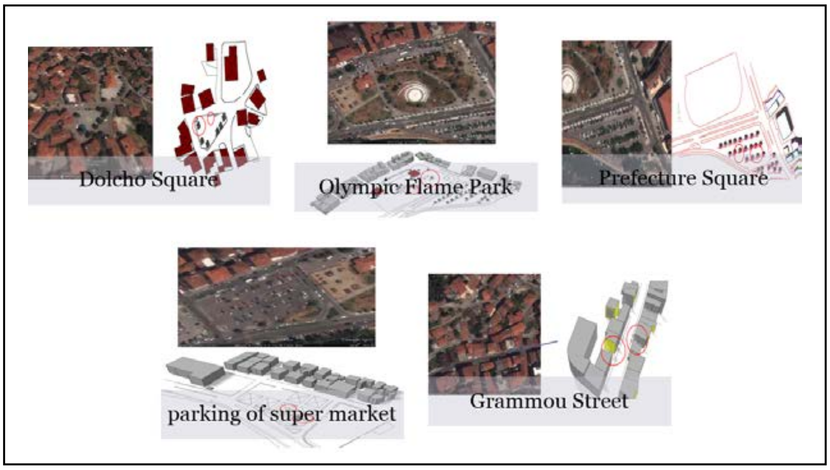


Figure 2: The Measurement Points

4. EXEMPLARY RESULTS AND DISCUSSION

Filling questionnaires, the thermal comfort conditions during morning, noon and afternoon time are investigated. A five scale graduation is used (very cold, cold, neutral, hot, very hot) in order to study the subjective comfort conditions. In Fig.3 the comfort conditions of Olympic Frame Park are observed, during 12-17 July.

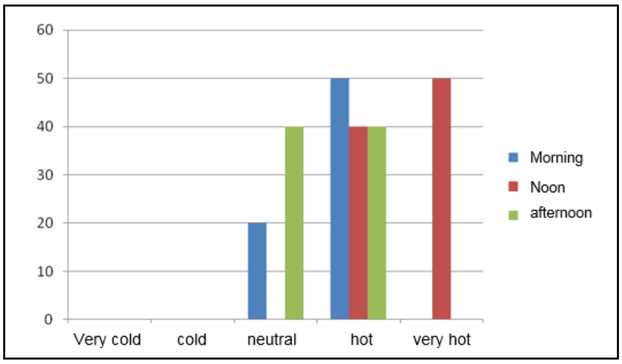


Figure 3:
Subjective comfort conditions
“Olympic flame” park, 40 persons

Just a few examples of the study can be presented hereafter:

In Fig. 4 the Surface Temperatures of covering materials in “Olympic flame” park (12-17/07) and the Tair over specific materials on height of 1.20 to 1.50m are observed [3], [4]. The Pv studio, Weather data analysis and Ecotect analysis are used in orer to simulate the conditons.

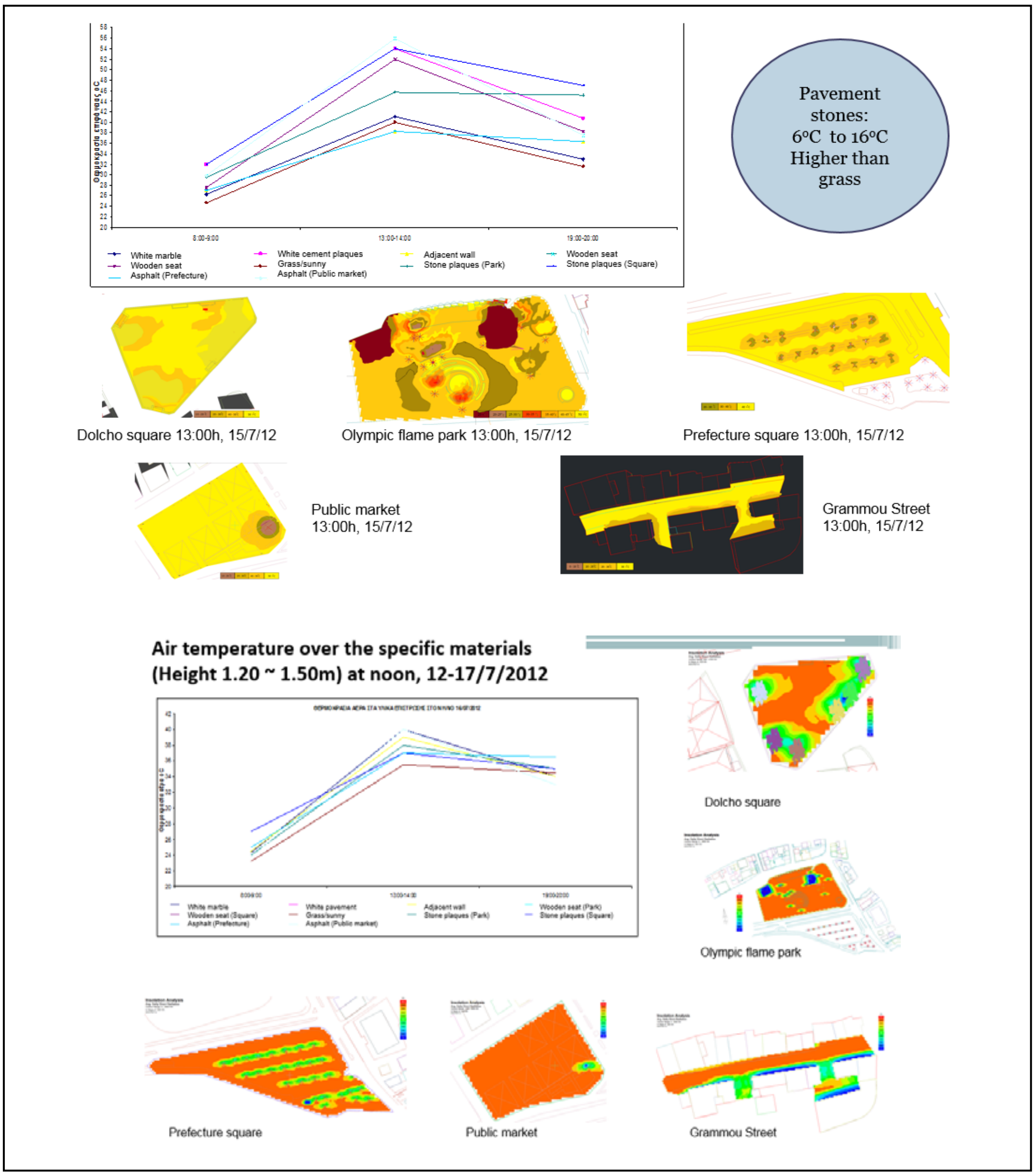


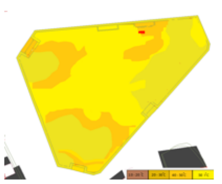
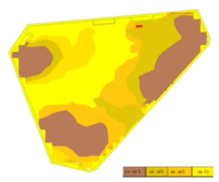
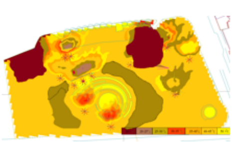
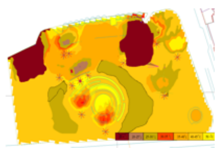
Figure 4: Surface Temperatures of covering materials (12-17/07)
and the Tair of specific materials on height of 1.20 to 1.50m

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After the analysis of Surface Temperature, Air Temperature and existing thermal conditions, a proposal for better comfort conditions is suggested. For example, the upgrading of the market square includes the replacement of the asphalt with perforated cement plaques, over grass, and/or just grass, and also trees that are planted along parking places and around the place. In Fig. 5 the results of the proposals are observed.

Public Market 15/7/2012												
hours	Tmrt (a)	Tmrt (b)	Tmrt (c)	PMV (a)	PMV (b)	PMV (c)	PET (a)	PET (b)	PET (c)	SET* (a)	SET* (b)	SET* (c)
8:00	53,8	52,0	49,8	3,6	3,6	2,4	40,4	40,5	34,6	33,7	33,9	26,1
13:00	66,3	63,0	62,4	6	5,1	5	51,8	47,7	46,9	42,5	38,7	37,5
20:00	27,6	27,7	27,6	2,8	1,7	1,7	33	29,3	28,6	22,9	20,5	19,4

(a) As measured
(b) Over proposed cool materials
(c) Over grass

Surface temperature (measured)	Surface temperature after the intervention	Tmrt (a)	Tmrt (b)	Tmrt (c)
Dolcho square 15/7/2012, 13:00 	Dolcho square 15/7/2012, 13:00 	65,4	52,8	52,9
Olympic Flame park 15/7/2012, 13:00 	Olympic Flame park 15/7/2012, 13:00 	65,2	63,4	64

Surface temperatures: as measured (b) over semi-covered ground (c) over simple grass

Figure 5: The results of the proposals

5. CONCLUSIONS

At the time of measurements (Mt):

An increase of the surfaces reflection causes decrease of the surface temperatures, but an increase of the MRT, PMV and PET, and as a result, worst comfort conditions.

An increase of the thermal capacity of materials, causes decrease of surface temperatures, MRT, PMV and PET, and as a result, better comfort conditions (Mt).

The replacement of hard materials with perforated materials, grass and trees, has as a result the better comfort conditions, as concluded from the decrease of 5^{o}C in the air temperature.

The replacement of the materials has decreased MRT, PMV, PET & SET in comparison with the existing situation.

The replacement of the asphalt at the large parking places with perforated materials or grass, has as a result a significant improvement of the comfort condition indices in both simulations, and we observe an exceptional improvement in the case that we replace the existing asphalt with grass on soil...

By comparing all the data gathered, it has been concluded that the replacement of the usually used in Greek open spaces materials (asphalt, concrete, stones) with perforated materials or grass,

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and the plantation of specific kinds of trees, improves largely the thermal comfort conditions of the urban microclimate and of course, of the specific places.

This research project has studied thermal comfort conditions in open spaces by on site measurements, questionnaires, use of software and has led to proposals towards the improvement of the conditions.

References

[1] Matzarakis, A. και H. Mayer (2008). Dependence of the thermal urban climate on morphological variables. Ber. Meteor. Inst. Univ. Freiburg 17, 129-139.

[2] Nikolopulou, M., N.Chrisomallidou, K. Steemers, R. Compagnon, J. Kang, N. Kofoed,G. Scudo, και L. Katzschner (2004). Rediscovering the Urban Realm and Open Spaces (RUROS), 2001-2003. Key Action 4, "City of Tomorrow and Cultural Heritage", from the program "Energy, Environment and Sustainable Development", within the Fifth Framework Program of the EU. ISBN: 960-86907- 2-2

[3] Kosmopoulos P., Kameni D., (2014). Sustainable interventions in urban public places, IC2 Urban Heat Island, Venice

[4] Kantzioura A., Kosmopoulos P., (2014). Surface temperature behavior of covering materials and comfort conditions. Energy in Buildings, ASHRAE, Athens

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Environmental sustainability for an existing airport

S. Aksit Sahinkaya, F. Germirli Babuna*

Department of Environmental Engineering, Istanbul Technical University, 34469, Istanbul, Turkey
*Corresponding author: Email: germirliba@itu.edu.tr

Abstract

The aviation sector is the by far the most improved mode oftransportation among the others. According to the International Air TransportAssociation (IATA), global passenger traffic is raised by 5.9 % from 2013 to2014. Such an increase shows the growth of demand in air travel. The same association states that aviation is responsible of 2% of the global carbon dioxide emissions. Significant amounts of fossil fuels are consumedand the growing problems of greenhouse gas emissions and subsequent climatechange are contributed by virtue of the aviation. The environmental impacts ofthe aviation industry not only come from aircrafts, but also from airports andtheir supporting infrastructure. Thus, environmentally sustainable airports mustbe considered as an inseparable part of sustainable aviation systems. In thiscontext, the objective of this study is to evaluate an existing airport interms of its carbon footprint and to put forth recommendations on developingthe environmental sustainability of the facility. For this purpose SabihaGokcen International Airport, located in Istanbul is investigated. According to 2014 data, more than 23.5 million passengers are used the airport and about 185400 flights are realized annually. The amount of waste and wastewater generationand information on their management/treatment practices, energy requirement forbuildings (heating and cooling), fuel consumption of airplanes, fuelrequirement for air-side vehicles and shuttles used for employeetransportation, the amount of used deicer are gathered for the last threeyears. The mentioned information is fed to ACERT v3.1 calculation tool toobtain the carbon footprint of the facility. Currently a 2nd runway is underconstruction. This runway will be completed in 2017. Due to this elevation in capacity greenhouse emissions are estimated to increase three fold. To tackle with thisrecommendations that develop the sustainability of the airport are presented.

Keywords: airport; carbon footprint; greenhouse gasses; sustainable development.

1. INTRODUCTION

The aviation sector is the by far the most improved mode of transportation among the others. According to the data of International Air Transport Association (IATA), global passenger traffic expressed as revenue passenger kilometres is raised by 5.9 % from 2013 to 2014 [1]. According to the projections, till 2030 an exponential growth is expected in global airline revenue passenger kilometres that corresponds to the product of number of passengers and the distance they travelled [2]. The realized increase and projections show the drastic growth of demand in air travel. On a global basis currently the aviation sector is responsible for 2 % of all the anthropogenic carbon dioxide emissions [3]. The mentioned percentage is estimated to elevate up to about 15 % by the year 2050 [2,4]. Significant amounts of fossil fuels are consumed and the growing problems of greenhouse gas emissions and subsequent climate change are contributed by virtue of the aviation. On contrary to the general opinion, aviation generates 12 % of CO_2 emissions arising from all transportation sources whereas road transport accounts for 74 % [3]. The efficient usage of fuel is elevated by 70 % within the last 40 years due to new aircrafts [5]. It must be noted that the environmental impacts of the aviation industry not only come from aircrafts, but also from airports

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and their supporting infrastructure. Thus, environmentally sustainable airports must be considered as an inseparable part of sustainable aviation systems. Assessing the current environmental impacts of an existing airport is the prerequisite step in obtaining a sound roadmap towards sustainability for such facilities. A greenhouse reduction program can then be established on the results obtained.

In this context, the objective of this study is to evaluate an existing airport in terms of its carbon footprint. For this purpose Sabiha Gokcen International Airport, located on the Asian side of Istanbul is investigated.

2. MATERIALS AND METHODS

Similar to all other airports, various companies are running within Sabiha Gokcen International Airport complex. The first step in realizing the main task of this study that is evaluating the carbon footprint, is to set the boundaries. For this purpose both organizational and operational boundaries must be identified. Organizational boundaries defining which company operations should be included in greenhouse gas emission inventory can be established on three different approaches; namely equity share, financial control and operational control [6]. Among them operational control approach is selected for defining the organizational boundaries of the airport. Next step is to identify the operational boundaries that covers pointing out the emissions associated with the operations, grouping emissions as direct or indirect and categorizing the scopes of the emissions [6]. direct emissions are the ones generated from sources owned or controlled by the company. On the other hand, indirect sources are emissions resulting as a consequence of the activities of the company but occur at sources that are not owned or controlled by the company [6]. Airports Council International (ACI) categorizes the sources of emissions arising from airports under 3 scopes [7]:

i. Scope 1. Greenhouse gas emissions from sources that are owned or controlled by the airport operator. Scope 1 emissions are direct emissions.
ii. Scope 2. Greenhouse gas emissions from the off-site generation of electricity (and heating or cooling) purchased by the airport operator. Scope 2 emissions are grouped under indirect emissions.
iii. Scope 3. Greenhouse gas emissions from airport related activities from sources not owned or controlled by the airport operator. Similar to Scope 2 emissions, Scope 3 emissions are placed under indirect emissions.

Due to difficulties faced during data collection, terminal building and common facilities are taken into account for calculating the greenhouse emissions. It should be noted that there is a tri-generator in the airport. As the data related to the natural gas consumption of this tri-generator is not obtained, it is not included in the calculations. Fuel consumption of air-side vehicles and employee shuttles, the amount of waste/wastewater generation and information on their management/ treatment practices, amount of de-icer usage are considered within Scope 1 emissions. Scope 2 emissions cover purchased natural gas and electricity, whereas fuel consumption of aircrafts, fuel consumption of employee/visitor/passenger vehicles (private and public transportation) are defined as the sources of emissions under Scope 3. Data gathered for the years 2012, 2013 and 2014, are fed to Airport Carbon and Emissions Reporting Tool (ACERT v3.1 calculation tool) [8] developed by ACI to obtain the carbon footprint of the facility for the mentioned period.

3. LOCATION AND UTILITIES

Being the second biggest airport in Istanbul, Sabiha Gokcen International Airport is serving for civil domestic and international flights. The general layout of Sabiha Gokcen International Airport is given in Figure 1.

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Figure 1. Bird's-eye view of Sabiha Gokcen International Airport [9]

Sabiha Gokcen International Airport is located on the Asian side of the city, about 50 kilometers away from the city centre (Taksim). It was opened to air traffic in 2001. It has one runway, four aprons, taxiways, a tower, an entrance control building, domestic and international terminal buildings, a cargo terminal, a hangar, a customs office building, a site for fuel, a wastewater treatment plant, a luggage handling and control system, a fire station, a police building, a regulator building, a power centre, a heating and cooling plant and a solid waste collection and separation centre [10].

3. RESULTS AND DISCUSSION

Currently Sabiha Gokcen International Airport provides service to 23.6 million passengers annually. Figure 2 illustrates the changes in number of flights and passengers with years. As can be seen from the figure, a rapid rise in the usage of the airport is observed.

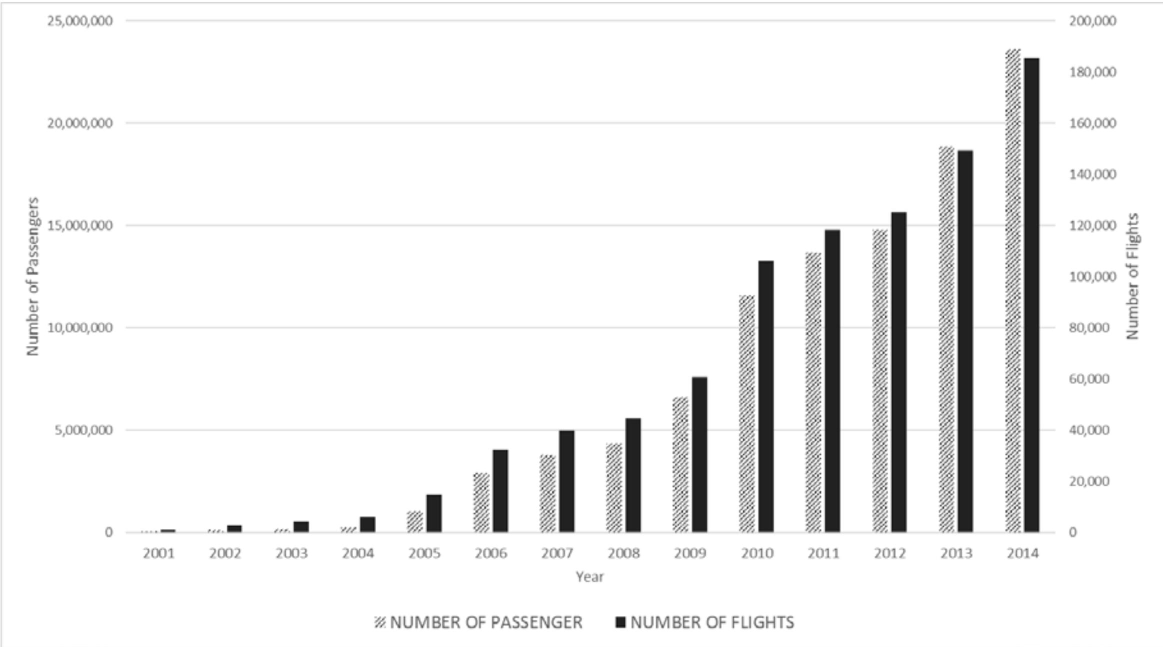


Figure 2. Total annual number of flights and number of passengers from 2001 to 2014

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A high amount of water is required to run an airport. Quite a fraction of this water input is used for non-potable quality demanding points such as landscape irrigation, vehicle washing, pavement cleaning etc. Therefore, grey water treatment and reuse, is applied in some airports to reduce the amount of water consumption.

An index showing the amount of water consumption per passenger is used for denoting the level of water used in airports. Table 1 outlines the mentioned index for various airports. This index indicates water conservation practices applied in the airport up to a level. However, it is also affected from various factors i.e. attitude of the people using the airport, amount of cargo transportation so on. As can be seen from the table a high level of water consumption per passenger is given for Narita airport, although grey water from terminal restaurants are used for toilet flushing [11]. The lowest figure is stated for Atlanta airport where water saving sanitary equipment and an air cooling system running without water cooling towers are used [11]. Due to the presence of rain water collection system and water saving sanitary equipment, Frankfurt airport also has a low water consumption [11]. Similarly, a low level of water consumption per passenger is associated with Sabiha Gokcen International Airport. Such a low figure is obtained because all the treated wastewater is reused for irrigation of the landscape.

Table 1. The amount of water consumption per passenger for various airports

Airport	Annual number of passengers (millions)	Water consumption (lt/passenger)	Reference
Atlanta International	89	11	[11]
Brussels	17.2	15	[11]
Ataturk	53.3	16	[13]
Frankfurt	53	17	[11]
Porto	5.3	17	[11]
Sabiha Gokcen	23.6	17	This study
Paris Orly	25.2	19	[11]
Zurich	22.9	23	[11]
Madrid Barajas	49.8	24	[11]
Tancredo Neves	9.5	27	[12]
Amsterdam	45.2	27	[11]
Munich	34.7	28	[11]
London Heathrow	65.9	28	[11]
Sydney	36	29	[11]
Toronto	31.8	29	[11]
Rome Fiumicino	36.2	32	[11]
Paris Charles de Gaulle	58.2	39	[11]
Lizbon	14.1	43	[11]
San Francisco	39.3	46	[11]
Manchester	18.3	50	[11]
Narita	32.9	53	[11]

Electricity consumption is an important source of greenhouse gas emissions. Usually the emissions arising from electricity consumption for a country is calculated on the basis of composite electricity-heat emission factors (unit CO_2 emissions per kWh) put forth by International Energy Agency (IEA) [14]. ACERT v3.1 calculation tool uses emission factor of IEA's 2011 data to calculate carbon footprint due to electricity consumption. The amount of purchased electricity for

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Sabiha Gokcen International Airport shows 23% increase from 2012 to 2014. On the other hand these figures indicate a 76 % decrease in CO_2e emissions per passenger in electricity usage within the given period of time.

Fuel consumption of aircrafts, fuel requirement for the transportation of staff/visitors /passengers to the site are considered while defining Scope 3 emissions. Calculations on Scope 2 emissions are based on purchased electricity and purchased natural gas. Scope 3 emissions has the highest share within all CO_2e emissions. After Scope 3, Scope 1 emissions that consist of fuel usage by air-side vehicles and employee shuttles, de-icer usage and waste/wastewater management, are observed to be the highest contributor of CO_2e emissions. Both Scope 2 and Scope 3 emissions are indirect ones, therefore it is not possible to control or lower them with the measures taken by airport operators. Percent distribution of emissions for 2014 are illustrated in Figure 3.

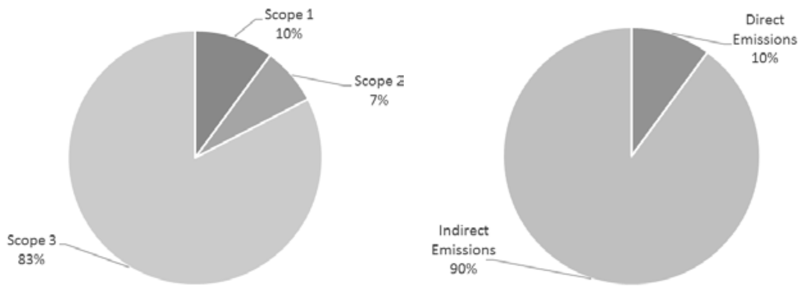


Figure 3. Percent distribution of emissions

Figure 4 shows CO_2e emissions of Sabiha Gokcen International Airport from 2012 to 2014.

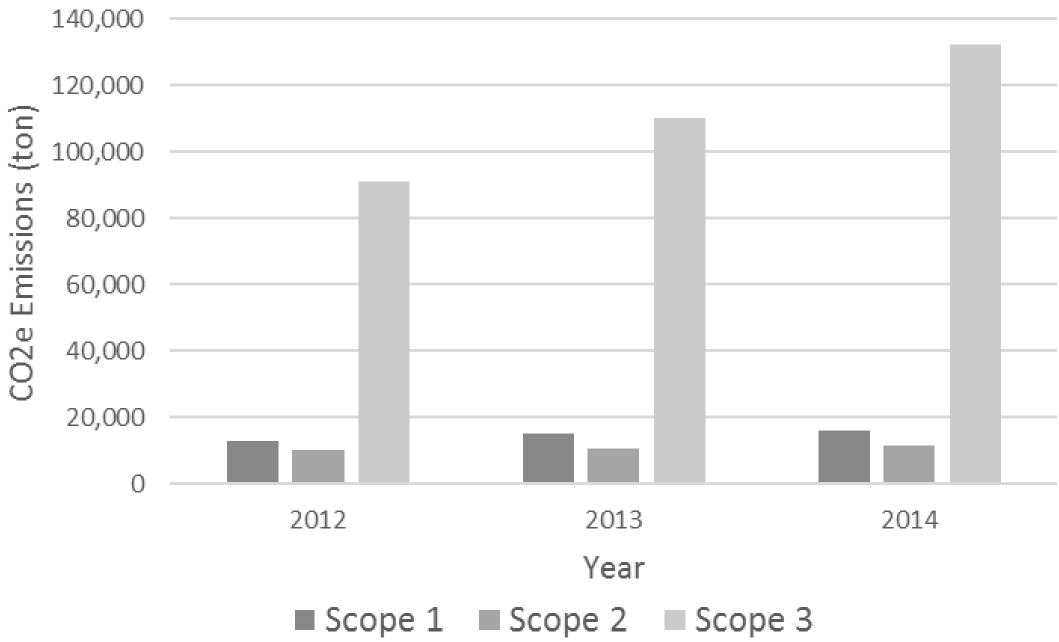


Figure 4. CO_2e emissions for 2012, 2013 and 2014

Scope 1 emissions are the most important ones as these constitute the directly controllable group. Emissions arising from Scope 1 activities for 2012, 2013 and 2014 are given in Figure 5. Among all Scope 1 emissions, de-icer usage (glycol) is the highest contributor, where after fuel usage by air-side vehicles and employee shuttles come. Calculations based on year 2014 show that

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67.8 % of the Scope 1 emissions arise from de-icer usage, 26.5 % from fuel usage by air-side vehicles and employee shuttles and finally 5.7 % from waste management.

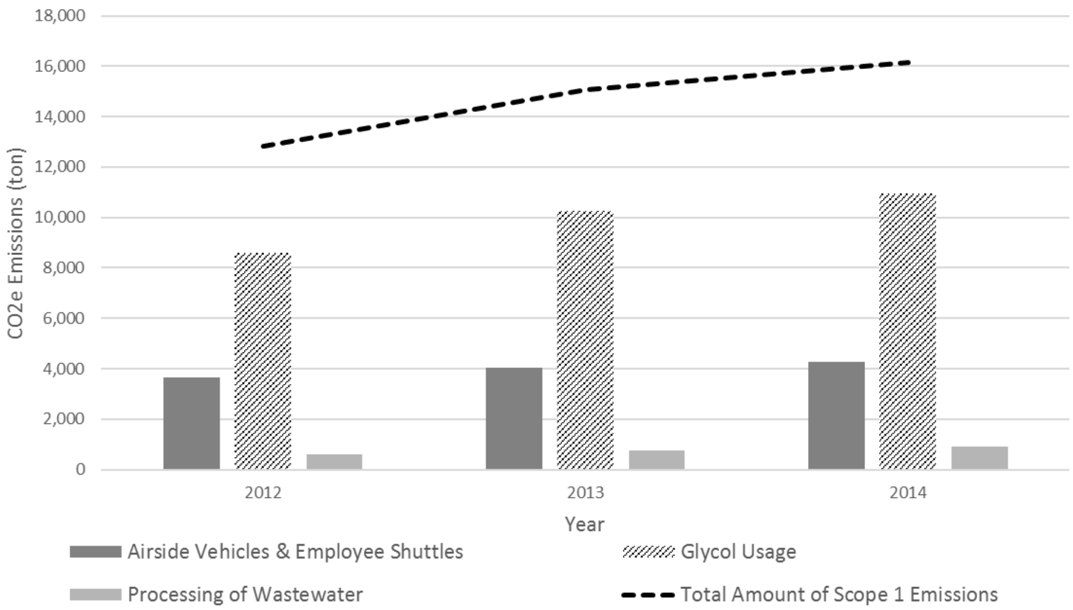


Figure 5. CO_2e emissions from Scope 1 activities

Percent distribution of Scope 1 and Scope 2 emissions for 2014 is given in Figure 6. Among these scopes de-icer (glycol) usage is assessed to be the highest CO_2e emitting source with an approximate percentage of 39. After that electricity input; and fuel usage of air-side vehicles and employee shuttles come.

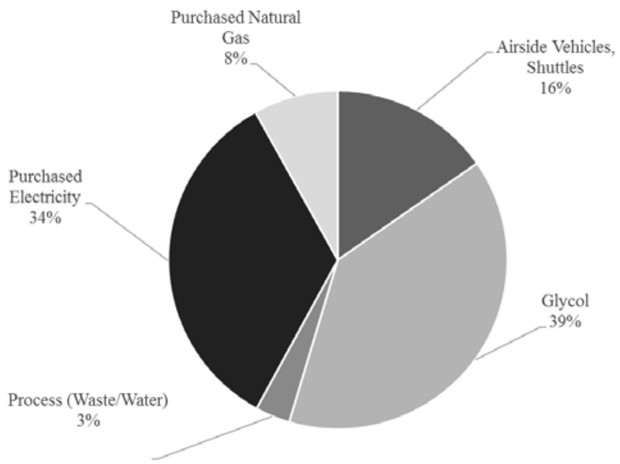


Figure 6. Distribution of Scope 1 and Scope 2 emissions for 2014.

Annual total CO_2e emissions and kilogram CO_2e per passenger values obtained for 2012, 2013 and 2014 are illustrated in Figure 7.

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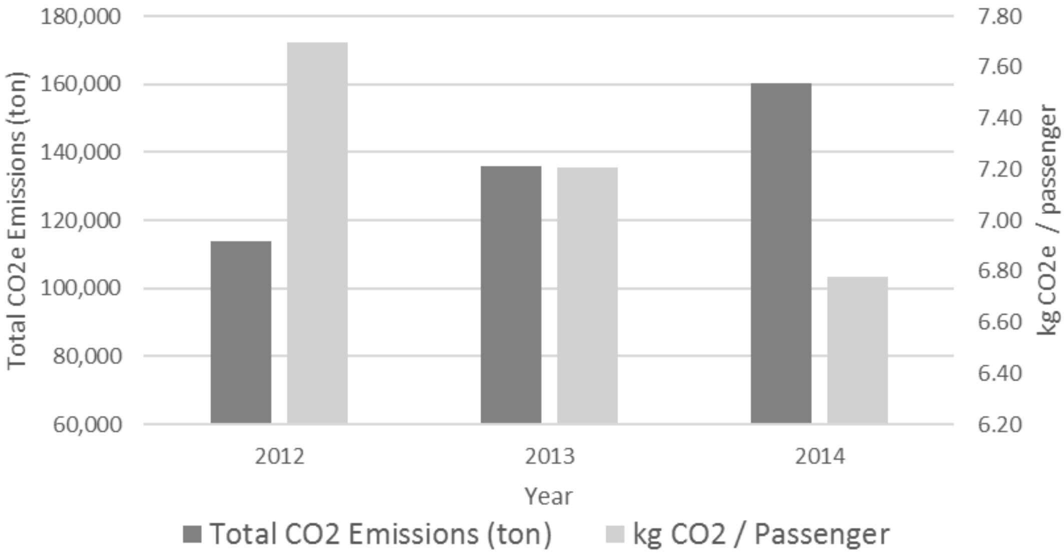


Figure 7. Total CO_2e emissions and kilogram CO_2e per passenger values for 2012, 2013 and 2014

Figure 7 shows a 40 % increase in total CO_2e emissions generated by the airport from 2012 to 2014. However, a decreasing trend from 7.70 to 6.78 is obtained for kg CO_2e emissions per passenger within the same period of time.

CONCLUSIONS

The concluding remarks obtained from this study that investigates the carbon footprint of Sabiha Gokcen International Airport are summarized below.

i. The airport has quite a low water consumption of 17 litre per passenger as a result of reusing all the treated effluents for landscape irrigation.
ii. The total CO_2e emissions arising from the airport are increased by 40 % from 2012 to 2014. On contrary to this elevation, a reduction from 7.70 to 6.78 CO_2e emissions per passenger is observed within the same period of time.
iii. It is recommended to concentrate further studies on reducing the controllable emissions such as energy requirement of air-side vehicles and employee shuttles, de-icer usage etc.

References

[1] IATA, 2015. Healthy April Passenger Demand**,** Press Release No. 22 http://www.iata.org/pressroom/pr/Pages/2015-06-04-02.aspx (accessed February 1, 2016).

[2] Baxter, G., Wild, G. and Sabatini, R., 2014. A sustainable approach to airport design and operations: Case Study of Munich Airport. *Practical Response to Climate Change*, Engineers Australia, Convention 2014, 25-27 November, Melbourne.

[3] ATAG, 2015. Air Transport Action Group. http://www.atag.org/facts-and-figures.html (accessed February 28, 2016).

[4] Whitelegg, J. and Cambridge, J., 2004. *Aviation and Sustainability- A Policy Paper*, Stockholm Environment Institute, ISBN 91 88714 91 8.

[5] Postorino, M. N. and Mantecchini, L., 2014. A transport carbon footprint methodology to assess airport carbon emissions. *Journal of Air Transport Management*, **37**, 76-86.

[6] http://ghgprotocol.org/ (accessed February 1, 2016).

[7] ACI (2009). *Guidance Manual: Airport Greenhouse Gas Emissions Management*, Airport Council International, 1st Edition, November.

[8] http://www.aci.aero/About-ACI/Priorities/Environment/ACERT (accessed February 1, 2016).

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[9] https://goo.gl/maps/iMSY9R4psz62 (accessed February 1, 2016).
[10] Detam, 2013. *Environmental Impact Assessment (EIA) Report of 2nd Runway for Sabiha Gokcen Airport*.
[11] Carvalho, I. C., Calijuri, M. L., Assemany, P. P., Silva, M. D. F. M., Neto, R. F. M., Santiago, A. F. and Souza, M. H. B., 2013. Sustainable airport environments: A review of water conservation practices in airports. Resources, *Conservation and Recycling*, **74**, 27-36.
[12] Couto, E. A., Calijuri, M. L., Assemany, P. P., Santiago, A. F. and Lopes, L. S., 2015. Greywater treatment in airports using anaerobic filter followed by UV disinfection: An efficient and low cost alternative. *Journal of Cleaner Production*, **106**, 372-379.
[13] Kilkis, S. and Kilkis, S., 2016. Benchmarking airports based on sustainability ranking index. Journal of Cleaner Production, in press.
[14] http://www.iea.org/publications/free_new_Desc.asp?PUBS_ID=2143 (accessed September 1, 2011).

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Assessment tools for energy efficiency in the tertiary sector buildings

S. Tournaki[1], T. Tsoutsos[1*], M. Frangou[1], Z. Urosevic[2]

[1]Technical University of Crete, School of Environmental Engineering, Renewable and Sustainable Energy Systems Lab, Chania, Crete, Greece.
[2]World Tourism Organisation, Madrid, Spain.
*Corresponding author: Email: theocharis.tsoutsos@enveng.tuc.gr

Abstract

The lack of certification and commonly acknowledged assessment tools results to limited investors' confidence in energy efficiency projects. To counter this, the European initiativeTrust EPC South is developing an investment standardization and benchmarking framework to technically appraise existing tertiary sector buildings and to evaluate the environmental impact and alternative energy efficiency actions. It is built upon an established real estate assessment tool, the Green Rating™ building assessment tool. The resulting framework will be tested on more than 40 pilot projects in 6 countries (Portugal, Spain, France, Italy, Croatia and Greece). Specifically for the hospitality sector, another online solution -the neZEH e-tool- aspires to motivate and support hoteliers towards becoming more energy efficient and transforming their hotels into nearly Zero Energy Buildings. The tool benchmarks the hotel’s current energy performance providing suggestions for energy efficiency measures, taking into account local parameters.

Keywords: energy efficiency assessment tools; nearly zero energy buildings; nZEB; high energy efficient hotels; Energy Performance Contract

1. INTRODUCTION

The services (tertiary) sector includes activities related to trade, finance, real estate, hospitality, health, education, and commerce. Energy consumption in the sector increased significantly in the early 2000s and showed a trend for decline after 2008 as a result of the European policies and the Members States regulatory measures to increase energy efficiency, also due to the economic recession. The most recent European Directive 2012/27/EU foresees 20% reduction of overall energy consumption [1]. However, at present, there is insufficient public and private investment in Energy Efficiency (EE).

Nevertheless, a different trend is observed in several southern, eastern and Mediterranean countries that show an increase in energy intensity. The data suggest that there is a significant potential for energy efficiency improvement, especially in these countries. However, several financial and other non-technical barriers hamper the fulfillment of such investments. One of the main barriers is the difficulty in accessing financing due to limited investors' confidence. The lack of proper certification, validation, and assessment tools are the main factors causing that. Energy Performance Contracting (EPC) is a way to boost private energy efficiency investments, but still lighthouse projects are rare in the tertiary sector of southern European countries to trigger replications.

To counter this, Trust EPC South [2], a project co-funded by the European Union’s Horizon 2020 Research and Innovation Programme, is developing an investment standardisation and benchmarking framework, which is able to technically appraise existing tertiary sector buildings and evaluate the environmental impact and energy efficiency actions that can be undertaken. It built upon an established real estate assessment tool (Green Rating™) and offers a pragmatic and cost-

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effective approach: an assessment, benchmarking and decision-making tool based on six environmental criteria and four levels of performance. Weighting the 3 quantitative indicators (energy, carbon, water) and the 3 qualitative ones (transport, wellbeing, waste) the tool delivers a benchmarkable rating to compare the sustainability performance of buildings and decide the most cost-effective measures to undertake. During the project`s lifespan, the existing methodology will be adapted and upgraded, by covering tertiary sector buildings and energy efficiency solutions that can be applied to them and including a financial assessment model. The resulting framework will be tested on at least 40 pilot projects in 6 countries (Portugal, Spain, France, Italy, Croatia and Greece) aiming to become a reference tool for such investments assessment and decision-making processes.
For the hospitality sector in specific, another online solution, the neZEH [3] e-tool, to be used by hoteliers themselves, aspires to motivate them and support their decision making towards becoming more energy efficient and transforming their hotels into nearly Zero Energy Buildings (nZEB). The neZEH e-tool has been upgraded by the nearly Zero Energy Hotels (neZEH) initiative, a project co-funded by the Intelligent Energy Europe Programme of the European Commission, that aimed at accelerating the rate of the refurbishment of existing hotels into nZEB. The neZEH e-tool benchmarks the hotel's current energy performance and provides suggestions for energy efficiency measures, taking into account local parameters, such as prices and climate.

This paper presents the tools developed in the framework of the European initiatives Nearly Zero Energy Hotels and Trust EPC South and the experience gained in Greece and other EU countries.

2. TOOL FOR GREEN BUILDING CERTIFICATION

The suitable certification, validation and assessment tools are key factors for bank financing. In order to technically value the existing tertiary sector buildings and evaluate the environmental impact and EE actions that can be undertaken, is exploiting the Green Rating™ methodology. This one, designed first and foremost by property practitioners for the real estate sector, offers an assessment, benchmarking and decision-making tool built on six environmental criteria (fig. 1) that provide results in monitoring and improving the sustainability performance of existing buildings.



Figure 1. The six objective indicators [4]

Its main features include:

- Third-party assessment by accredited certification bodies;
- Six tangible indicators (energy, carbon, water, transport, waste, wellbeing);
- Intrinsic actual performance (based on building components and systems under a standard scenario) and potential performance if Capital Expenditure -CAPEX- recommendations are implemented

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- Actual performance (based on actual consumption and operational practices) and potential with operational and behavioral changes
- A consistent methodology applicable across Europe.

The Green Rating™ indicators have been selected by experts and practitioners to best meet the demands of the real estate industry. The current Green Rating™ methodology covers the office, logistics, and retail sectors. Weighting the 3 quantitative indicators (energy, carbon, water) and the 3 qualitative ones (transport, wellbeing, waste) the Green Rating™ delivers a benchmarkable rating used internationally by its clients to compare the sustainability performance of buildings and decide the most cost-effective measures to undertake.

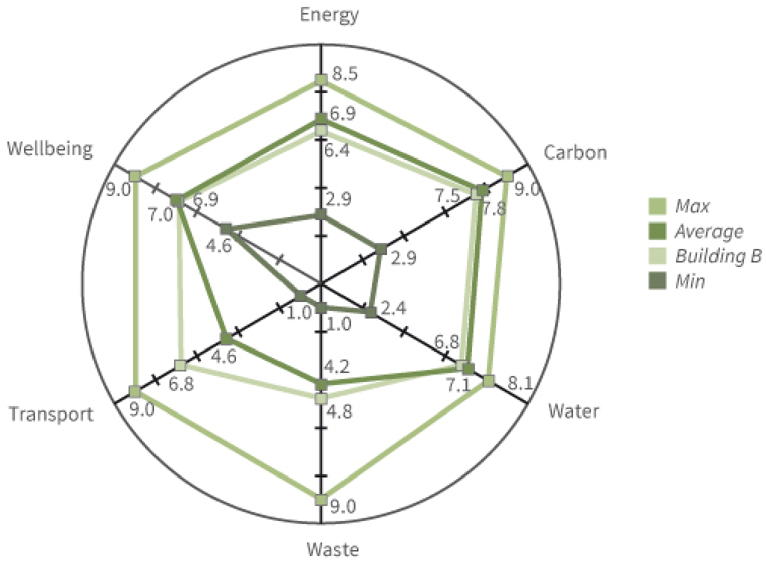


Figure 2. Example of Building B in Frankfurt, Germany [4]

For the purpose of the Trust-EPC-South project [5, 6], the existing Green Rating™ methodology is planned to be upgraded as a sustainable energy investment assessment and benchmarking tool addressing building and facility renovations. The first step shall be its adaptation for the covered tertiary sector segments (such as hospitality, healthcare, leisure centres, theatres, etc.). This means the development of assessment criteria and relevant indicators for specific buildings and other types of facilities [7].



Figure 3. Illustration of the Trust-EPC-South benchmarking approach [2]

Successively, our next step is to refine and expand the Green Rating™ Methodology for the specific benchmarking purpose of the Trust-EPC-South project. Primarily, this shall mean the inclusion of a financial assessment model to complement the existing technical Green Rating™ assessment. The integration of this financial assessment model shall complement the existing technical methodology and create a holistic score for EPC project benchmarking.

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The final step will ensure that the project results are delivered to the market. This will be made possible thanks to the project consortium that will explore and define the best strategy to ensure the exploitation of the investment standardisation and benchmarking framework, and the generation of an additional pipeline of projects to be developed beyond the project's lifetime.

The tool will allow stakeholders to:

- improve understanding of the technicalities of energy efficiency and sustainable energy measures applied to buildings by modeling them, evaluating their cross effects and translating them into energy savings;
- appreciate the effects of implementing such measures not only within the energy dimension, but also across the other 5 Green Rating™ indicators: carbon, water, transport, waste and wellbeing;
- improve understanding of the economical and financial aspects of implementing such measures, in a language understandable by the financing side.

3. TOOL FOR ENERGY EFFICIENCY IN HOTEL BUILDINGS

The European initiative Nearly Zero Energy Hotels (neZEH), co-funded by the Intelligent Energy Programme of the European Commission, aims to accelerate the rate of the refurbishment of existing hotels to become nearly Zero Energy Buildings (nZEB). The main target is SME hotels, which represent 90% of the European hospitality market and are usually more reluctant to commit to energy saving measures and the use of renewable energies [8,9]. The neZEH initiative is a response to the European Directive on the Energy Performance of Buildings (2010/31/EU, EPBD recast), contributing directly to the EU 2020 targets and supporting EU Member States (MS) in their national plans for increasing the number of nZEBs, while supporting the European hotels to reduce their operational costs, to improve their image and services and so enhance their competitiveness.

The major outputs of neZEH are:

- An integrated set of decision support tools to assist hoteliers in identifying appropriate solutions and designing feasible and sustainable nZEB projects;
- An EU neZEH network to facilitate knowledge exchanging and cooperation between the demand (hotel owners) and supply side (building professionals);
- 16 demonstration pilot projects in 7 countries to act as "living" examples;
- Practical training and capacity building activities to support the implementation and uptake of nZEB projects;
- Integrated communication tools to promote front runners and to foster replication, challenging much more SMEs to invest in similar projects.



Figure 4. The 16 neZEH pilot hotels – lighthouse examples in Europe [3]

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The neZEH online e-tool [10] has been developed to support decision-making and motivate hoteliers wanting to refurbish their hotels to nZEB. The tool, based on the previously developed HES e-toolkit [11], has been upgraded to include the neZEH project approach and findings, among which the concept of nZEB in hotels as well as the assessment of all indicators towards nZEB, including carbon footprint. Its objective is to encourage engagement of and provide a basic but comprehensive overview for hotel owners and managers to help increase capacity in the accommodation industry to improve their energy performance by increasing energy efficiency and use of renewables. The e-tool is designed to encourage owners and managers to initiate projects of energy performance improvement in their hotels, the first steps of which are to commission an energy audit and obtain specialist technical advice appropriate to their particular building and circumstances, on how to set up and implement specific improvements in the energy performance of their premises.

The e-tool includes three main sections:

1. Assessment of the hotel's energy performance using a questionnaire in order to build an "energy use profile" of the hotel.
2. Identification of options for energy efficiency improvement on the basis of three main processes: elimination of energy use, reduction of energy use and substitution of non-renewable energy sources with renewable ones.
3. Awareness and knowledge section; τhis separate section includes inspiring examples by showcasing neZEH pilot hotels experiences.

The questionnaire includes four steps:

i. Step 1: Identification data – identification of the hotel and the reference year used for answering the questionnaire.
ii. Step 2: Hotel characteristics – gathers information about the climate zone where the hotel is located and the type of building; it further narrows the characteristics of the property by defining the energy management measures that are already implemented in the hotel.
iii. Step 3: Energy consumption - it continues to narrow the characteristics of the property by listing the energy sources used in the hotel and corresponding consumption patterns.
iv. Step 4: Energy profiling – final step aiming at understanding the efficiency of the hotel by presenting questions about the equipment and appliances installed in the hotel and establishing the potential for improvement into a more efficient facility.

When the user finishes the questionnaire, the tool provides the following reports as output:

1. Energy consumption report that includes: the hotel's current energy consumption ($kWh/m^2/y$), its current renewable energy share (%), the goals in order to become neZEH and the repartition of the hotel's energy consumption.
2. Energy solutions report including: measures to reduce energy consumption and increase the use of renewable energy, categorized in measures that are likely to be implemented and measures that need to be implemented in order to reach neZEH level, based on the hotel characteristics
3. Carbon footprint report that gives the current carbon footprint of the hotel ($kgCO_2/m^2$), both total and as a break-down per energy source used.

A Return of Investment calculator is also included, that can indicate the expected costs concerning investment, O&M and energy savings, helping in this way the hotelier decide in which technology project to invest. The Data Decision Support System (DSSS) of the e-tool is based on the back-end on an Excel Ranking Tool, which is able to rank energy efficiency measures for different types and categories of hotels at the country level, taking into account local parameters. The ranking is done based on four parameters (size of the financial investment, profitability, potential energy saving, European climate zones). It includes a list of energy efficiency measures, each of which is associated with a typical energy saving percentage (%), and modelled independently. Climatic data (heating and cooling degree days for the 28 EU Member States, heating and cooling needs, etc.) are

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taken into account and correction factors are used to adjust the potential energy savings percentage (%) depending on the climate zone.

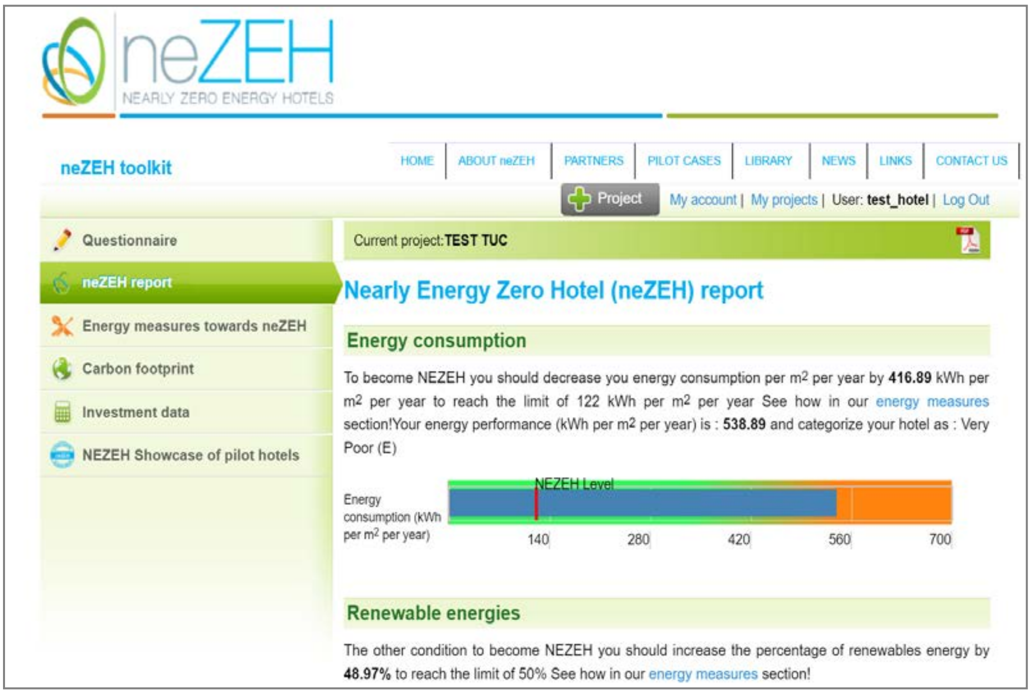


Figure 5. Energy consumption report from the neZEH e-tool [3]

The data are put together in four reference buildings and give as output, a ranking of energy efficiency measures in regard to three aspects:

1. Profitability of the financial investment in € invested per kWh saved ratio. The €/kWh saved ratio depends on the size of the financial investment in each country and the potential energy saving, which in its turn is affected by the correction factor for the climate zone.
2. The size of the financial investment in €. The cost of each measure depends on the selected country.
3. Potential Energy Saving in kWh/y from each technology. The kWh/y saved is also affected by the correction factor for the climate zone.

In Figure 3, a detailed flux diagram of the Excel Ranking Tool is presented. The tool needs five inputs (A1a-e) in the topics: Energy, Buildings, and Economics. In order to get the ranking, both kWh saved and €/measure are required, shown as red squares in the flux diagram. The energy saved per measure is calculated mainly by three inputs: the typical energy saving percentage per measure (A1a), the climate in the country (A1b) and energy balances (A1c). The first two are subordinated to several specific parameters which work as correction factors; the correction factors are based on different modelling for every measure. The third is given by a database of energy balances included in the tool. The energy balances, extracted from real hotel energy audits, were contributed by the neZEH partners. A correction factor for the energy saved has been developed to adjust it to some climates. As the last step, there is a need for the model to establish some reference buildings (A1d) in order to have fixed energy consumption (A6). The estimation of €/measure is based on a partnership-contributed prices database (A1e) which includes €/unit (i.e. €/LED lamp, €/Boiler etc.) and the labor cost per country.

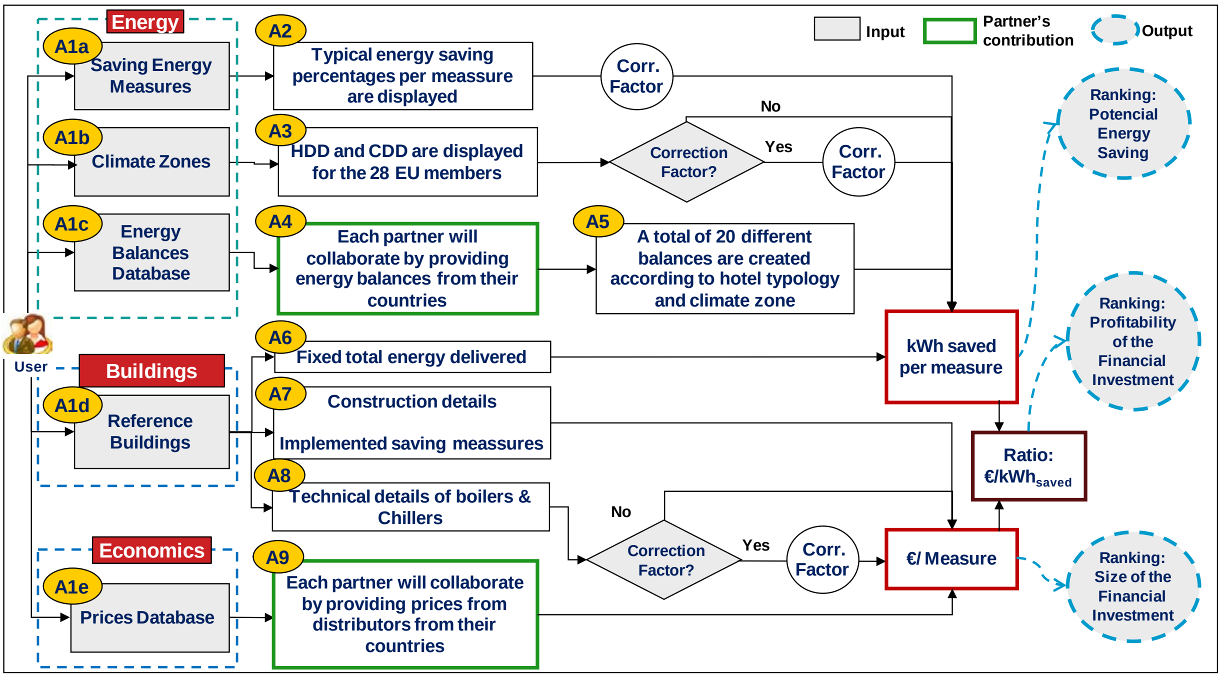


Figure 6. Flux diagram of the back-end Excel Ranking Tool [12], [13]

4. CONCLUSIONS

Achieving the European Union's 2020 energy efficiency targets and at the same time reducing its dependency on energy imports is a huge task that requires innovative approaches and tools - such as the Green Rating and neZEH tools - to foster investments into sustainable energy by:

a) increasing the confidence of the tertiary sector investors through standard evaluation methodologies and accompanying project developers in the economical and technical project structuring,
b) providing decision-making assistance in evaluating carbon emissions and mitigation techniques and ranking practical and cost-effective energy efficiency and renewable energy investment options.

The developed tools can support scaling up investments in sustainable energy technologies in the private tertiary sector providing credible, standard methods to value EE projects under different perspectives (economic, social and environmental), which ultimately will facilitate decision-making process and build confidence in the decision making and financing institutions.
Finally, both tools will contribute to build skills among the financial sector in the evaluation and assessment of investments in EE/RES.

ACKNOWLEDGMENTS

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References

[1] Directive 2012/27/EU of the European Parliament and of the Council of 25 October 2012 on energy efficiency Official Journal L315/1, 14.11.2012

[2] TRUST-EPC-SOUTH - Building TRUST in Energy Performance Contracting for tertiary sector energy efficiency and sustainable energy projects in Southern European Countries, www.trustepc.eu (accessed April, 2016).

[3] neZEH – nearly Zero Energy Hotels, www.nezeh.eu (accessed April, 2016).

[4] Green Rating, www.green-rating.com (accessed April, 2016).

[5] Various. Overview EPC Market Insight Report, www.trustepc.eu/en (accessed April, 2016).

[6] Tournaki S., Tsoutsos T., Farmaki E., Sonvilla P., 2016. Building trust in Energy Performance Contracting in Southern European countries – the Trust EPC South project. *Proceedings of the 5th International Conference on Renewable Energy Sources & Energy Efficiency,* 5-6 May 2016, Nicosia, Cyprus.

[7] Tsoutsos T., Tournaki S., Farmaki E., Sonvilla P., Lensing P., Bartnicki J., Cobos A., 2016. Benchmarking framework to encourage energy efficiency investments in South Europe. The Trust EPC South approach, *Proceedings of the SBE16 Thessaloniki "Sustainable Synergies from Buildings to the Urban Scale" International Conference, October 17-19, Greece.*

[8] Tsoutsos, T., Tournaki, S., Avellaner de Santos, C., Vercellotti., R., 2013. Nearly Zero Energy Buildings. Application in Mediterranean hotels. *Energy Procedia*, 42, 230 - 238.

[9] Tsoutsos T., Tournaki S., Urosevic Z., Derjanecz A., Nunez C., Pouffary S., Morell R., Claridge N., Mauro S., Rata C., Biscan M., 2013. Nearly Zero Energy Hotels - NEZEH, *Proceedings of the AIVC conference, Energy conservation technologies for mitigation and adaptation in the built environment: the role of ventilation strategies and smart materials*, September 25-26, Greece.

[10] neZEH e-tool, www.nezeh.eu (accessed May, 2016).

[11] Hotel Energy Solutions (HES), http://hotelenergysolutions.net/ (accessed December, 2015).

[12] Tsoutsos T., Tournaki S., Frangou M., Urosevic Z., Derjanecz A., Rata C., Morell R., Bišćan M., Pouffary S., Levi Sacerdotti S., Claridge N., Núñez C., 2016. Demonstrating Nearly Zero Energy Hotels in Europe - Examples and experiences from the European initiative neZEH, *9th International Conference Improving Energy Efficiency in Commercial Buildings and Smart Communities*, March 16-18, Frankfurt, Germany.

[13] S. Tournaki, M. Frangou, T. Tsoutsos, I. Guerrero Hernandez, A. Derjanecz, J. Kurnitski, A. Litiu A., T. Buso, Nearly Zero Energy Hotels – From European Policy to Real Life Examples: the neZEH Pilot Hotels. Proceedings of the 3rd International Conference "Energy in Buildings 2014" (Athens, Greece, 15 November 2014). ISSN: 2241-9748.

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Assessing urban mobility conditions through the use of indicators: The case of the Pylaia-Panorama and Pavlos Melas municipalities

K. Tselepidou[1], Z. Choris[1], A. Sdoukopoulos[2*], F. Kehagia[3]

[1]Department of Science and Technology, Hellenic Open University, 26335 Patra, Greece.
[2]Transport Engineering Laboratory, Department of Civil Engineering,
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
[3]Highway Engineering Laboratory, Department of Civil Engineering,
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece.
*Corresponding author: Email: asdoukop@civil.auth.gr

Abstract

Sustainable Urban Mobility Plans (SUMPs) are being considered as an ambitious policy tool aiming to improve urban mobility and the quality of life of citizens in urban areas in terms of social equity, economic efficiency and environmental integrity. Since SUMPs were first introduced in European transport policy, in 2009 through the "Action plan on Urban Mobility", more and more cities are being encouraged to initiate the process of implementing a SUMP. While in Greece few cities have actually implemented a SUMP, this number is expected to increase substantially during the next years as it will soon become a precondition for cities for continuing to receive state financing. According to the guidelines that have been developed for successfully implementing a SUMP, the assessment of the current situation in a city is the first critical point that needs to be taken into careful consideration. The assessment of a city's urban mobility conditions can be undertaken by using a variety of tools and a set of targeted indicators. The latter are being considered as a valuable tool for presenting and assessing a city's urban mobility conditions as they are simple to use and can efficiently communicate complex phenomena to citizens in a comprehensive way. Within the framework of this paper, an assessment of the urban mobility conditions of two municipalities i.e. the Pylaia-Panorama and the Pavlos Melas municipalities located in the Thessaloniki region in Greece, was undertaken using a set of 45 sustainable urban mobility indicators as defined based on an extended literature review. The methodological approach as well as the tools used to measure each indicator (e.g. in situ measurements, questionnaire surveys, collection, organization and analysis of GIS databases, etc.) are being briefly described within this paper and the respective results are being analyzed highlighting the strengths and weaknesses of the urban transport system in the two aforementioned areas. The results of the assessment also enabled to draw interesting conclusions regarding the existing conditions of urban mobility in those two areas thus define specific goals and interventions that have to be undertaken in order to pave the way towards the successful implementation of a SUMP there in the near future.

Keywords: sustainable urban mobility indicators; municipality of Pylaia-Panorama; municipality of Pavlos Melas; SUMP

INTRODUCTION

The conventional transport planning approach being implemented during the last decades although attempted to cope with the increased transport demand by constructing additional road infrastructure yet imposed further pressures on the operation of the transport system such as traffic congestion, air pollution, traffic noise, visual disturbance and degradation of the environment. The aforementioned phenomena highlight thus the emergence of adopting a contemporary sustainable

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transport planning approach focusing on the encouragement of sustainable modes of transport i.e. walking, bicycle and public transport, and the provision of mobility and information services. Towards this direction, Sustainable Urban Mobility Plans (SUMPs) are being considered as an ambitious policy tool aiming to improve urban mobility and the quality of life of citizens in urban areas in terms of social equity, economic efficiency and environmental integrity. Since SUMPs were first introduced in European transport policy, in 2009 through the "Action plan on Urban Mobility", more and more cities are being encouraged to initiate the process of implementing a SUMP [1]. While in Greece few cities have actually implemented a SUMP, this number is expected to increase substantially during the next years as it will soon become a precondition for cities for continuing to receive state financing. According to the guidelines that have been developed for successfully implementing a SUMP, the assessment of the current situation in a city is the first critical point that needs to be taken into careful consideration. The assessment of a city's urban mobility conditions can be undertaken by using a variety of tools and a set of targeted indicators. The latter are being considered as a valuable tool for presenting and assessing a city's urban mobility conditions as they are simple to use and can efficiently communicate complex phenomena both to citizens and other stakeholders in a comprehensive way. Moreover, according to several authors, indicators enable to monitor progress towards a specific goal or objective such as sustainable urban mobility whilst they also facilitate the identification of significant trends and the comparison of different time periods and urban areas sharing similar features [2, 3, 4]. Furthermore, indicators contribute to setting policy priorities as well as to ranking potential measures and interventions [5].

Within the framework of the current research, an assessment of the urban mobility conditions of two municipalities planning to implement a SUMP during the next years (as it is outlined by their short-term business plans) namely the Pylaia-Chortiatis and the Pavlos Melas municipalities located in the Thessaloniki's metropolitan area in Greece, was carried out using a set of 45 sustainable urban mobility indicators adapted to the specific features of the reference area. The development of the aforementioned indicator set was based on an extended literature review as well as on the widely accepted selection criteria such as the relevance to sustainability and transport-related policies, the simplification, the transparency and the accessibility of the indicators to all stakeholders, the increased sensitivity that enables to highlight even slight changes, the compatibility between different jurisdictions as well as the continuity, availability, frequency and reliability of the necessary original data [5, 6].

Regarding the reference area, the city of Thessaloniki comprises a major cultural, commercial, financial and political centre of greater Balkans while it constitutes the administrative centre of the region of Central Macedonia and the second largest urban area of Greece in terms of area, population and economic activity. In specific, the metropolitan area of Thessaloniki extends over an area of 1.455 km^2 and as outlined by the recent (2011) census it accommodates approximately 1.000.000 citizens [7]. Moreover, according to the latest relevant datasets (2016) available from the International Monetary Fund, the area of Thessaloniki contributes to the Greek Growth Domestic Product (GDP) by a significant share which corresponds to 8,6% [8]. As far as the main features of the examined municipalities are concerned, Municipalities of Pylaia-Chortiatis and Pavlos Melas are located in the Northeast and Northwest region of the Thessaloniki's metropolitan area respectively consisting of the 6^{th} and 3^{rd} largest municipalities in terms of population. Residential constitutes the prevailing land use in both cases while the commercial zone extends along certain road axis such as Prof. Ilia St. and Davaki St. respectively. Concerning the traffic features, private car is considered as the dominant transport mode while urban buses operated by the Organisation of Urban Transportation of Thessaloniki consist of the only means of public transport. Moreover, total absence of bicycle infrastructure is being observed in both areas. The selected set of sustainable urban mobility indicators is presented in Table 1 below.

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Table 1: Presentation of the developed set of sustainable urban mobility indicators

ID	Indicator
1.Integration of land use/transport planning	
1.1	Total area
1.2	Population
1.3	Population density
1.4	GDP per capita
1.5	Unemployment rate
1.6	Land use mix
1.7	PT network coverage
1.8	Distance between successive PT stops
1.9	Access to basic services
1.10	Private car ownership
2.Effective traffic and parking management	
2.1	Modal split
2.2	Occupancy rates of passenger vehicles
2.3	Traffic congestion (delay)
2.4	Average speed of private vehicles
2.5	Road network density
2.6	Road safety
2.7	Sense of security
2.8	Affordability (share of income devoted to transport)
3.Promotion of bicycle and walking	
3.1	Pedestrian infrastructure density
3.2	Cycling infrastructure density
3.3	Share of streets with traffic calming measures
3.4	Cycle parking availability
3.5	Share of sidewalks which are wheelchair accessible
3.6	Road safety and vulnerable users
4.Promotion of Public Transport	
4.1	Average age of PT fleet
4.2	PT frequency
4.3	Hours of service
4.4	Average PT speed
4.5	PT comfort
4.6	PT security
4.7	Capacity of Park and Ride facilities
4.8	PT affordability
4.9	PT size in relation to population
4.10	Occupancy rate of PT vehicles
4.11	Share of PT stops with shelter
4.12	Share of smart PT stops
4.13	Share of PT vehicles which are wheelchair accessible
4.14	Annual trips per capita with means of PT
4.15	PT network density
5.Promotion of "green" technologies and measures	
5.1	Share of vehicle fleet meeting certain air emission standards
5.2	CO_2 emissions per mode
5.3	CO_2 emissions per type of fuel
5.4	Total CO_2 emissions
5.5	Share of vehicle fleet
5.6	Share of hybrid private vehicles

The methodological approach as well as the tools used to measure each indicator (e.g. in situ measurements, questionnaire surveys, collection, organization and analysis of GIS databases, etc.) are being briefly described within this paper and the respective results are being analyzed

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highlighting the strengths and weaknesses of the urban transport system in the two aforementioned areas. The results of the assessment also enabled to draw interesting conclusions regarding the existing conditions of urban mobility in those two areas thus define specific goals and interventions that have to be undertaken in order to pave the way towards the attainment of sustainable urban mobility.

References

[1] Commission of the European Communities, 2009. Action plan on Urban Mobility. COM(2009) 490/5, Brussels.

[2] Gilbert, R., Irwin, N., Hollingworth, B., Blais, P., 2003. Sustainable Transportation Performance Indicators (STPI). *Transportation Research Board*.

[3] Litman T.A., 2009b. *Sustainable transportation indicators: a recommended research program for developing sustainable transportation indicators and data*. In Transportation Research Board 88th Annual Meeting (No. 09-3403).

[4] Haghshenas, H., Vaziri, M., 2012. Urban sustainable transportation indicators for global comparison. *Ecological Indicators*, **15(1)**, 115-121.

[5] Dobranskyte-Niskota, A., Perujo, A., Pregl, M., 2007. *Indicators to assess sustainability of transport activities Part 1: Review of the Existing Transport Sustainability Indicators Initiatives and Development of an Indicator Set to Assess Transport Sustainability Performance*. European Commission, Joint Research Centre.

[6] Zheng, J., Garrick, N.W., Atkinson-Palombo, C., McCahill, C., Marshall, W., 2013. Guidelines on developing performance metrics for evaluating transportation sustainability. *Research in Transportation Business & Management*, **7**, 4-13.

[7] www.statistics.gr (accessed April 8th, 2016).

[8] www.imf.org (accessed April 8th, 2016).

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A sustainable energy and development pattern based on R.E.S. for insular and rural communities

D. A. Katsaprakakis[1*], D. Zafirakis[2], D. G. Christakis[1], J. Kaldellis[2]

[1] Wind Energy and Power Plants Synthesis Laboratory, Department of Mechanical Engineering, Technological Educational Institute of Crete, 71410, Estavromenos, Heraklion, Crete, Greece.
[2] Laboratory of Soft Energy Applications and Environmental Protection, Technological Educational Institute of Piraeus, Building C, Room Γ015, 250 Thivon & Petrou Ralli Ave. 12244 Aegaleo, Athens.
*Corresponding author: Email: dkatsap@wel.teicrete.gr

Abstract

The optimum approach for achieving sustainable development of insular and rural communities is not based on either the prolongation of fossil fuels' use, or the "anarchic" invasion of huge R.E.S. power plants in sensitive ecosystems or limited territories. Sustainable development should be approached with the introduction of energy saving and rational use of energy techniques in buildings, premises and transportation sector, the introduction of central or decentralized electricity production power plants, involving R.E.S. and energy storage technologies and the participation of the local population, the local authorities and local investors or investment schemes.
In this paper, the above described development pattern is presented for the Aegean Sea island of Sifnos, implemented by the local Energy Cooperative with the support of the Municipality, aiming to guarantee a 100% annual R.E.S. penetration in the island's energy overall consumption.

Keywords: *insular and rural communities sustainable development; hybrid power plants; distinct heating cooling conditioning; smart grid; rational use of energy*

1. INTRODUCTION

1.1. The remote power systems in Greece

A large number of remote power systems, located in insular territories, are met in Greece. These systems exhibit similarities regarding the power consumption, the currently developed economic activities and the resulting status of the local economies, the availability of Renewable Energy Sources (R.E.S.) potential and specific development perspectives.

In figure 1 the annual electricity consumption curve is presented for the island of Sifnos, located in the eastern part of the Cyclades complex, with a permanent population of around 2,500 residents. The seasonal variation of the power demand is clearly depicted in this figure, a feature most commonly met in all the Greek autonomous power systems. In this specific island, the power demand during summer is measured approximately three times higher than the averaged one during the rest seasons, a fact imposed exclusively by the multiplied activities in the island in summer due to the tourist sector. Actually, tourist sector consists the main pillar for the local economy, representing more than 80% of the annual income of the local community and supplying the fundamental funding base for a number of small local commercial enterprises. This power demand intensive seasonal variation between winter and summer period is mainly met in medium and small size power systems, with strong dependency on tourist economy. In cases of larger islands, such as Crete, Lesvos etc, with local economies further developed in several sectors apart from the tourist one (agriculture, small industries etc), the power demand seasonal variation is less intensive [1, 2].

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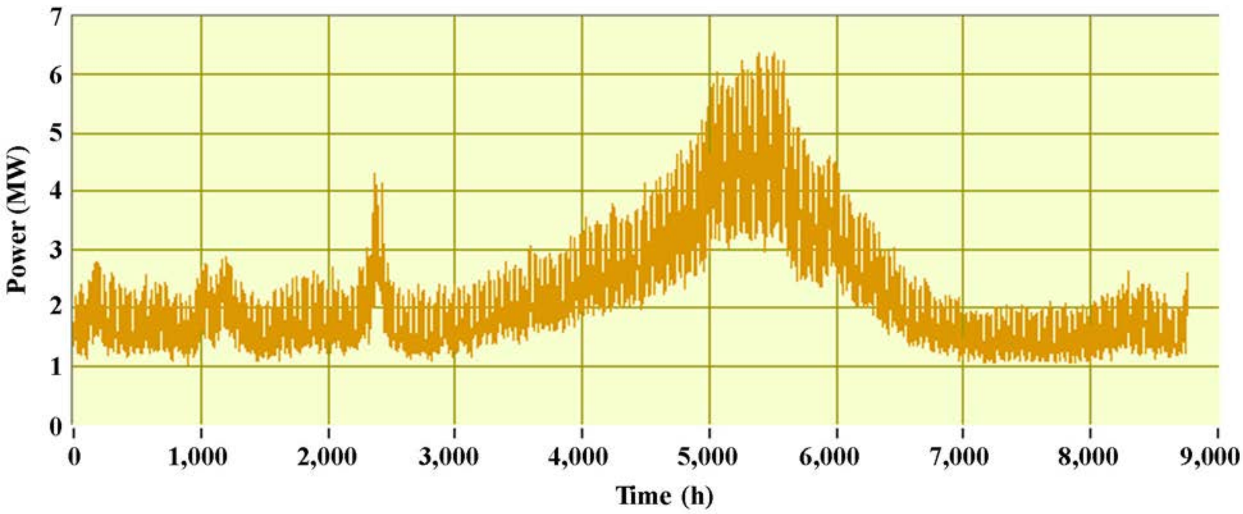


Figure 1: Annual electrical power demand in the island of Sifnos estimated for the year 2020.

Currently all the energy needs in the Greek islands are covered by imported fossil fuels, specifically heavy fuel in larger islands for electricity production and diesel oil, almost in all islands, for peak power production and transportation sector. Annual specific electricity production costs range from 0.15 €/kWh in the larger islands to 0.25 €/kWh in smaller ones, while in some cases of very small islands, with some tens of permanent population, this feature may exceed 1 €/kWh. Tremendous amounts are spent annually for these fossil fuels imports. In Crete, for example, every year more than 300,000,000 € are required only for the consumed fossil fuels in the electricity sector.

Another fundamental characteristic of the insular territories in Greece is the rich R.E.S. potential. The R.E.S. potential in Greece – mainly the wind potential and the solar radiation – has been evaluated during the last thirty years with hundreds of measuring stations. The results of these stations indicate that Greece should be placed among the richest countries in the world, regarding the available primary energy sources [3-6]. Annual averaged wind velocities higher than 10 m/s are often measured in the insular country [3, 4], while the annual global irradiation is recorded higher than 1,900 kWh/m^2 [5, 6]. The annually available R.E.S. potential in the Greek insular territory outgrows the annual electric [7, 8], thermal and mechanical energy demand and, additionally, can be a fundamental exportable product, capable of becoming the locomotive lever for the recovery of the Greek national economy, starting from the local ones. Consequently, the available R.E.S. in Greece constitute a potential source of wealth which can boost the development of the country.

1.2. Exploitation of R.E.S. in Greece: a bad beginning

Currently, not only the existing R.E.S. potential in the Greek islands remains unexploited, but, in addition, an anarchic policy has been adopted by the investors since 2009, regarding the submission of applications in Greece for the construction of electricity production projects from R.E.S. According to the official records of the Regulatory of Authority of Energy (the Authority in charge for the licensing of the submitted R.E.S. projects applications), the total licensed power exceeds 30 GW, while the annual maximum power demand in Greece varies around 11 GW. The total power of the submitted applications that still remain under evaluation is not easy to be calculated precisely. Roughly estimated, it must exceed 50 GW.

Another impressive point is the large number of applications and licenses for electricity production projects (mainly wind parks) of very large size (thousands of MWs) in the Greek islands [9]. Since the power demand in these insular systems is considerably lower than the total power of the submitted applications and the issued licenses, these applications and licenses also propose the

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interconnection of the insular systems with the mainland grid through underwater connection cables for the transportation of the produced power. Some characteristic applications – licenses in the Aegean Sea islands are listed below [10]:

- electricity production license from wind parks in the islands of Anafi, Astypalaia, Amorgos, Ios, with a total nominal power of 317.4 MW and existing annual peak demand of 68 MW
- electricity production license from wind parks in the islands of Kalymnos, Kos, Leros, with a total nominal power of 348 MW and existing annual peak demand of 90 MW
- electricity production license from wind parks in the island of Ikaria, with a total nominal power of 330 MW and existing annual peak demand of 8 MW
- application for electricity production license from wind parks in the islands of Milos, Kimolos, Sikinos, Folegandros, Astypalaia with a total nominal power of 93 MW
- licenses and applications in the island of Crete with total power around 5 GW, when the annual peak demand in the island is about 650 MW.

In many of the above described applications – licenses there are several violations of the restrictions defined in the national siting plan for the construction of electricity production power plants from R.E.S. Most of these restrictions usually aim at the protection of either environmentally sensitive geographical regions, such as sites of specific importance in Natura 2000 zones, or sites with special value for the Greek history, civilization and development, such as historical or cultural monuments and areas with distinguished natural beauty and considerable contribution to the local economies (beaches, national parks etc).

Additionally, the siting of these large scale projects in small geographical territories, such as the insular ones, often occupying all the available hills and mountains, certainly affects the existing human activities and turns the existing traditional attitude into an electricity production industrial area. It is obvious that, in case these projects are implemented, tourism, the one and only economic activity in these islands and the fundamental pylon of the Greek national economy, will collapse. Conclusively, the national economy will be dramatically affected, while the local economies will be totally destroyed. The natural environment will be also considerably affected.

Finally, in case of the exploitation of these large R.E.S. projects from a minority of investors, with the local communities totally absent, all the huge potential social and economic benefits that can be gained from R.E.S. projects in favor of the national economy and the local communities are simply lost [11, 12]. Simultaneously, the installation of these large projects will terminate any further possible development of R.E.S. projects in Greece, since all the available land and the electricity demand of the country will have been covered. So the perspective of the economic growth based on the exploitation of R.E.S. in Greece will be practically lost for ever and the country will be deprived one of the most promising prospects for a healthy, social and economic development.

2. FOCUSING ON A SUSTAINABLE ENERGY FUTURE

2.1. Energy saving

Any effort towards the approach of a sustainable energy future, which will boost the local economy development, should begin from the introduction of energy saving technologies in energy consuming processes. In Greek islands there is a huge potential for energy saving.

2.1.1. Passive solar systems in buildings – bioclimatic architecture

Bioclimatic architecture is strongly connected with the traditional insular architecture in Greece. Actually, it is the Greek insular territory the geographical region where the fundamental rules of the bioclimatic architecture are widely met in the 20th century. Large openings in the south walls to maximize solar radiation gains during winter, small openings in the north walls to ensure natural

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ventilation, exploiting, thus, the north-west breeze often blowing in the Aegean Sea during summer and outer walls with large width (usually larger than 0.50 m) to maximize the thermal resistance of the building's envelope constitute the most commonly met bioclimatic techniques in the Greek insular settlements.

Despite this architectural tradition, most hotels, erected in the early '80s, although the Greek Buildings Insulation Regulation does exist since 1979, were constructed without any fundamental passive measure, with the tolerance of the responsible Urban Planning Authorities, practically breaking the relevant legislation. The considerable increase of the cooling loads and the required primary energy consumption for the buildings conditioning was the direct consequence of this immature attitude.

Except envelope's insulation, further passive measures towards the reduction of the cooling loads can be the installation of double glazing with reflective coating in the building's openings, the construction of overhangs for the openings shading, the construction of green roofs, as well as more sophisticated measures, such as the introduction of openings in appropriate locations in the building's envelope to maximize natural ventilation (e.g. solar chimneys) and bioclimatic interventions of the surrounding environment aiming to increase the amount of latent heat versus the sensible one (water surfaces, planting areas etc).

Given the fact that a large amount of the cooling loads originates from interior space sources (human beings, electrical devices), the reduction of cooling loads from an adequate integration of passive solar systems in a building is estimated in the range of 20%.

2.1.2. Active systems for buildings conditioning

It was noted in the introductory section that electricity consumption in Greek islands exhibits much higher during summer, due to the extended tourist sector. This increase originates, to its larger percentage, from the energy required for buildings' conditioning, particularly hotels, studios etc. Currently, in the vast majority of the accommodation infrastructure, inner space conditioning is provided by air-to-air heat pumps of several types (VAV chillers, split units, etc), with averaged EER in the best case not higher than 2.0 – 2.5. From relevant accomplished studies regarding energy upgrade measures in hotels and studios, it is estimated that more than 50% (in some cases even 70%) of the annual electricity demand is consumed for the buildings conditioning.

Energy saving in buildings conditioning can be achieved mainly with the introduction of geothermal heat exchangers. The vicinity to the sea of the installation locations in most cases of large hotel groups enables the installation of open loop geothermal systems, operating with seawater pumped from the seawater aquifer, usually met a few meters under the ground. This guarantees the effective disposal of large amounts of cooling loads, without having to install some tens of kilometers of length of closed loop vertical geothermal heat exchangers, minimizing, thus, the imposed set-up cost. Indicatively, a specific set-up cost of 700 €/kW_{th} of final cooling load has been calculated for open loop geothermal heat systems in Greece. For closed loop vertical heat exchangers, this cost should be expected higher than 1,000 €/kW_{th}.

Geothermal systems are accompanied with water-to-water heat pumps, operating normally with averaged EER in the range of 4.5 to 5.0. Consequently, compared to the existing situation, an annual electricity saving of at least 40% should be expected.

2.1.3. Demand side management

On top of energy saving measures, demand side management (DSM) also comprises a critical element for achieving sustainable development in island regions. DSM, essentially suggesting control of electricity loads, covers a wide range of applications, extending from the residential to the transportation sector, and primarily aims to facilitate increased RES penetration without the need to oversize system components.

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DSM refers to both active and passive control of electricity loads, with the second one implying energy monitoring and proper signals (e.g. price ones) from the system operator side in order for consumers to willingly react by adjusting their consumption. On the other hand, active DSM suggests imposition of load control (load shedding or forced operation of loads, mainly secondary ones) in order to ensure efficient operation for power generation assets, exploitation of energy surplus and/or maintenance of sufficient energy stores in the case that energy storage is employed.

To this end, it is also important to stress association of DSM with energy solutions that are particularly suitable for island regions, like electrical vehicles (EVs) and desalination plants. Such applications could also be considered as DSM since they too suggest control of electric loads, mainly applied so as to exploit the energy surplus deriving from RES installations while also offering a clean solution to long-lasting problems of island regions.

On the other hand, when considering small and medium sized island regions, DSM becomes increasingly challenging. This is owed to the fact that in such electricity systems, the largest share of local loads normally corresponds to residential/hotel ones, while at the same time, load demand forecasting is extremely sensitive to sudden variations, owed to the absence of base loads like industrial ones.

As a result, detailed assessment needs to be carried out with regards to the classification of the different loads as elastic or inelastic ones. Such a classification could assess the DSM potential under different conditions of system operation and facilitate operation of a smart grid, where exchange of information takes place between the production and the demand side so as to optimize the overall system performance.

2.2. Electricity production from R.E.S.

Most islands in the world constitute power systems of medium or small size. The installation of electricity production power plants from R.E.S. in small insular systems is restricted due to dynamic security and stability constraints. Despite this fact, weak insular systems still constitute highly attractive regions for the development of electricity production power plants from RES, because of the available high wind potential and solar radiation [3-6], rarely met in the continental mainland and the high electricity generation specific cost from the existing autonomous thermal power plants [13, 14], favoring the economic feasibility of the RES electricity production projects.

The RES power penetration restrictions imposed in insular systems for dynamic security and stability reasons are encountered with the combined operation of RES and storage power plants. The overall RES – storage power plants are commonly known as “hybrid power plants”.

The size of the hybrid power plant is imposed by the power demand size of the insular system. The size of the hybrid power plant will determine, in turn, the RES and storage technologies that should be employed. The technically mature and economically competitive available technologies are:

- RES units: wind parks and photovoltaic stations;
- storage power plants: Pumped Storage Systems (PSS), Compressed Air Energy Storage (CAES) systems, electrochemical batteries, electrolysis units for hydrogen production.

PSS constitute the more mature storage technology of large size and occasionally of medium size (annual peak demand higher than 2 MW), while electrochemical storage is ideal for small size applications (peak demand lower than 1 MW). CAES constitute a relatively new technology. For the time being, there are two conventional CAES systems operating, one in Neuen Huntorf, Germany and one in McIntosh, U.S.A.

The introduction of hybrid power plants in insular non-interconnected power systems has constituted a popular concept in the research literature during the last three decades. A hybrid power plant is usually introduced into a power system aiming at the following:

- to support high RES power plants penetration, maximizing the exploitation of the locally available RES potential;
- to reduce the consumption in the energy sector of the, usually imported, fossil fuels;

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- in case of autonomous insular systems, to reduce the frequently existing high electricity generation cost;
- to strengthen the local economy;
- to improve the energy security of remote geographical regions.

Aegean Sea islands are blessed with abundant wind, sun, sea and intensive land morphology. Given these conditions, they constitute ideal territories for wind parks and seawater PSS hybrid power plants in cases with peak power demand higher than 2,5 MW. This minimum size is normally adequate to ensure compensation of the high infrastructure works set-up cost of a PSS. In case of Sifnos, for example, the local Energy Cooperation has begun the licensing procedure of a wind powered PSS with a wind park of 12 MW nominal power and a seawater PSS with 1,100,000 m^3 upper reservoir capacity, 320 m net head, 7 MW of hydro turbines and 10 MW of pumps installed power. The above dimensioning can fully support the electricity demand as it is estimated in 2020 (approximately 18.5 GWh), adopting an annual increase rate of 1.5%, leading to 100% of RES penetration over the annual electricity consumption. This achievement constitutes a major target of the local Energy Cooperation. The total set-up cost of this system is estimated at 35,000,000 €, while the produced electricity selling price should be around 0,25 €/kWh, configured on the basis of the electricity production specific cost of the existing thermal power plant, as defined in the relevant legislation. Given these facts and a funding scheme of 35% equities and 65% loan capitals with a loan rate of 6.5% and a payback period of 10 years, the equities payback period is calculated at 6 years and the corresponding IRR at 18%.

3. APPROACHING A FEASIBLE DEVELOPMENT PATTERN

Keeping the island of Sifnos as a case study, the construction and the operation of the hybrid power plant will simultaneously lead to a reduction of the annual expenses for the electricity production, currently afforded by the local network operator and to the implementation of a feasible and profitable investment, with an annual net income for the local Energy Cooperation of 3,000,000 €. In figure 2, the stored water volume annual variation in the PSS upper reservoir is presented. It is seen that there is a considerable time percentage (specifically 1,216 hours annually) during which the upper reservoir is full. This means that during this time period any potential power surplus from the hybrid station's wind park will not be possible to be stored, leading to an estimated annual electricity rejection of 13 GWh (roughly 33% of the annual production from the wind park).

Instead of rejecting this electricity surplus, it could be exploited in newly introduced loads, such as desalination or electrical vehicles. Adopting an averaged specific electricity consumption for potable water production through a reverse osmosis process of 4 kWh/m^3, it is estimated that these 13 GWh of electricity surplus, once exploited in desalination units, will permit an annual potable water production of 3,250,000 m^3. This quantity of available fresh water in a community of 2,500 permanent residents will create a huge potential for the development of new activities in the island, based on the exploitation of the locally available sources and the possibilities offered by the excellent local climate conditions, such as the biological growth of agricultural products and the implementation of pilot farms of biological husbandry, beekeeping etc. The introduction of these new activities in the island's local economy will require the disposal of some initial capitals for the construction of the required infrastructure (e.g. potable water storage reservoirs, hydraulic networks, housing of the new enterprises etc). These capitals can be provided by the hybrid power plant's net profits. Consequently, by re-investing a percentage of the annual net profits of the hybrid power plant for the creation of the required infrastructure, new trades and professions can be introduced in currently unexploited sectors, creating thus serially new occupation positions and strengthening the local economy by introducing additional alternative professional options, instead of the currently economic structure, based almost exclusively on tourism.

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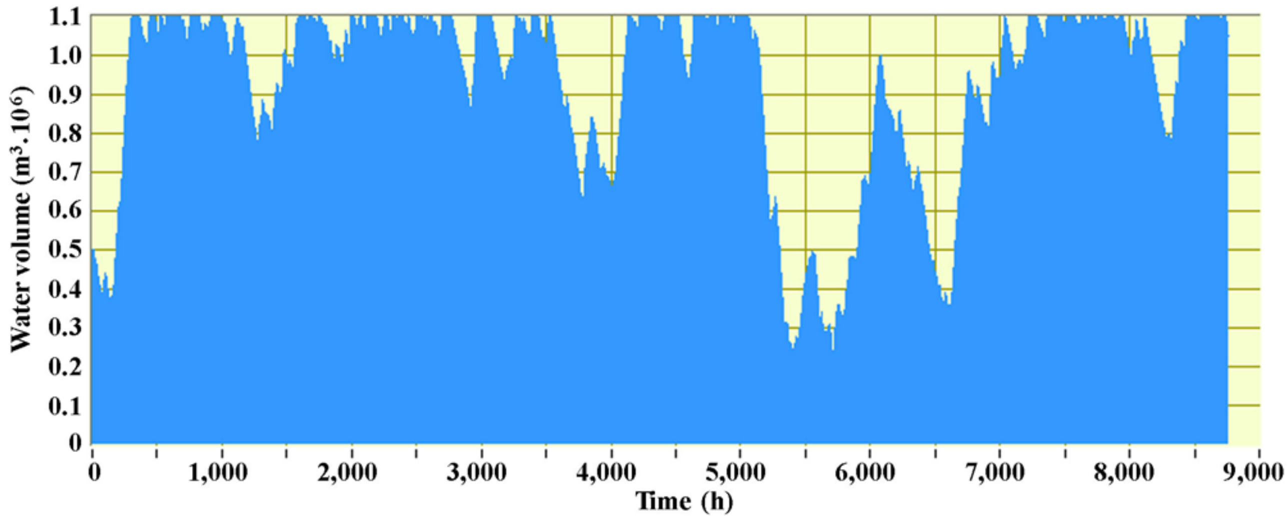


Figure 2: Annual variation of stored water volume in the PSS upper reservoir for the case of Sifnos.

Additionally, by introducing the energy saving available possibilities described previously, it is estimated that at least an annual reduction in the electricity consumption of 40% can be achieved. This reduced electricity consumption will offer the ability to import new loads in the insular system, such as electrical vehicles or the new electricity consumptions imposed by the newly introduced economic activities. Finally, the overall energy balance between energy saving, energy production from the R.E.S. power plant and the new mixture of energy consumptions will be fulfilled by achieving simultaneously the energy independency and security of the insular community, based on the exploitation of the locally available R.E.S. potential and the offered energy saving techniques. Any import of primary energy sources will be eliminated. This new energy balance is depicted graphically in figure 3.

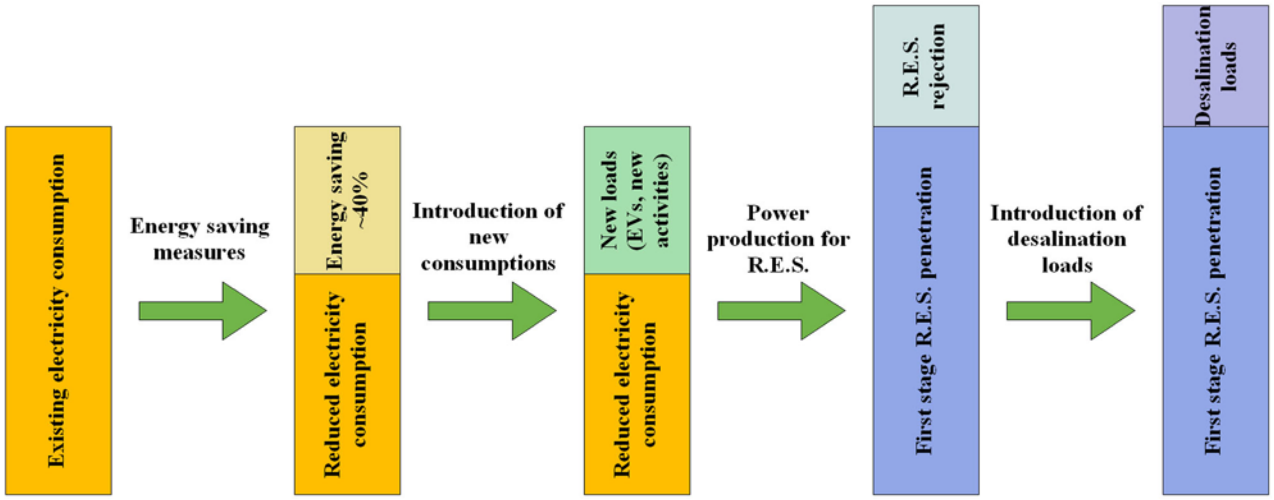


Figure 3: Energy balance between energy saving, energy production from R.E.S. and new loads.

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4. CONCLUSIONS

In this article the perspective towards a sustainable and feasible development pattern based on the exploitation of R.E.S. potential in insular and remote communities was presented. Energy Cooperatives, local Municipalities and investors figure as the ideal schemes for the implementation of this approach. Given the initiative of the Energy Cooperative in the Aegean Sea island of Sifnos, characteristic features were presented for this particular case, proving the feasibility of this plan and revealing the huge imposing development potential. A fundamental state support is an apparent prerequisite for the successful implementation of such efforts. Specifically in the case of Greece, this implies, first of all, the recall of all the issued licenses for large wind parks projects in the insular territories or the rejection of the similar pending applications. Furthermore, the existing legislation should be adapted to conclude to a clear and integrated supporting framework for the promotion and the licensing acceleration of R.E.S. projects originated from local investing schemes.

REFERENCES

[1] Katsaprakakis D. Al., Papadakis N., Christakis D. G., Zervos A, 2007. On the wind power rejection in the islands of Crete and Rhodes. *Wind Energy*, **10**(**5**), 415–434.

[2] Kaldellis J. K., Zafirakis D., 2007. Present situation and future prospects of electricity generation in Aegean Archipelago islands. *Energy Policy*, **35**(**9**), 4623-4639.

[3] Kanellopoulos D., 1992. National wind resources validation in Greece. *Journal of Wind Engineering and Industrial Aerodynamics*, **39**(**1-3**), 367-372.

[4] Kotroni V., Lagouvardos K., Lykoudis S., 2014. High-resolution model-based wind atlas for Greece. *Renewable and Sustainable Energy Reviews*, **30**(**38**), 479-489.

[5] Flocas A. A.. 1980. Estimation and prediction of global solar radiation over Greece. *Solar Energy*, **24**(**1**), 63-70.

[6] Photovoltaic Geographical Information System (PVGIS)
http://re.jrc.ec.europa.eu/pvgis/cmaps/eu_cmsaf_opt/G_opt_GR.png
(accessed 17/4/2016).

[7] Xydis G., 2013. Comparison study between a Renewable Energy Supply System and a supergrid for achieving 100% from renewable energy sources in Islands. *International Journal of Electrical Power & Energy Systems*, **46**(**22**), 198-210.

[8] Katsaprakakis D. Al., Christakis D. G., 2009. Maximisation of R.E.S. penetration in Greek insular isolated power systems with the introduction of pumped storage systems. *Proceeding of the European Wind Energy Conference and Exhibition 2009*, March 16-19, Marseille, France, Vol. 7, 4918-4930.

[9] R.A.E. G.I.S map: http://www.rae.gr/geo/ (accessed 17/4/2016).

[10] Katsaprakakis D. Al., Christakis D. G., 2016. The exploitation of electricity production projects from Renewable Energy Sources for the social and economic development of remote communities. The case of Greece: An example to avoid. *Renewable and Sustainable Energy Reviews*, **54**(**16**), 341-349

[11] Silvina Belmonte, Karina Natalia Escalante, Judith Franco, 2015. Shaping changes through participatory processes: Local development and renewable energy in rural habitats. *Renewable and Sustainable Energy Reviews*, **45**(**22**), 278-289.

[12] Frank Pieter Boon, Carel Dieperink, 2014. Local civil society based renewable energy organisations in the Netherlands: Exploring the factors that stimulate their emergence and development. *Energy Policy*, **69**(**27**), 297-307.

[13] Gustavo A. Marrero, Francisco Javier Ramos-Real, 2010. Electricity generation cost in isolated system: The complementarities of natural gas and renewables in the Canary Islands. *Renewable and Sustainable Energy Reviews*, **14**(**9**), 2808-2818.

[14] Daniel Weisser, 2004. On the economics of electricity consumption in small island developing states: a role for renewable energy technologies? *Energy Policy*, **32**(**1**), 127-140.

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The contribution of the marine and coastal environment in the quality of resident's life in the city of Kavala

S. Tampakis[1], T. Panagopoulos[2*], P. Karanikola[1], P. Ypsilopoulos[1]

[1]Department of Forestry and Management of the Environment and Natural Resources, Democritus University of Thrace, 193 Pantazidou street, Orestiada, Greece.
[2]Research Center for Spatial and Organizational Dynamics (CIEO), University of Algarve, Gambelas Campus, 8000 Faro, Portugal
*Corresponding author: Email: tpanago@ualg.pt

Abstract

The coast city of Kavala in northern Greece is a beautiful and productive place to live, work and visit to. In the view of residents, the sea constitutes a great advantage to this city. The present study examines residents' evaluation of the marine and coastal sectors to their contribution and perspectives of city development and quality life. Also evaluated the factors that mainly pollute the sea (aquatic and terrestrial) and the activities of different Stakeholders (State, Local Authorities, Scientific community, Ecological Organizations, citizens) to protect the marine environment from pollution. Face-to-face interviews were performed with 400 residents. The questionnaire was submitted to a factorial analysis of its validity and reliability. The results reveal that the most significant sectors for the development and quality of life in the city were tourism development of the coastal zone, the integration of the city landscape, fishery and oil extraction. Also important sectors were the attraction of cruise tourism the creation of jobs and transporting of people and goods. Even though the oil platforms were located in the marine environment, residents stated that the main factors of sea pollution are industry, domestic waste, pesticides and fertilizers. The least important appear to be rubbish and plastics, ship and oil spill accidents. Satisfaction for environmental activities was higher for ecological organizations and residents' community and less from State and Local authorities.

Keywords: *marine and coastal environment; aquatic and terrestrial pollution; citizens' views; stakeholder perceptions*

1. INTRODUCTION

The coastal zone is commonly defined as the interface for transition area between the land and the sea [1]. Many of the world's major cities are located in coastal areas and a large proportion of economic activities are concentrated in these cities [2]. 90% of the global fishery activity occurs in the coastal waters and coastal areas are the place where more than 45% of the world's population lives and works [3]. Greece is a maritime country with a coastline of over 15,000km. Most of the cities are located near the see, and Kavala is one of them with population 54,100 residents [4].

Coastal and marine ecosystems play a crucial role in supporting economic prosperity and social welfare in the adjacent human communities [5]. However, coastal areas and their ecosystems are subject to an increasing number of competing activities [6, 7]. Economic activities such as fishing, aquaculture, tourism, energy production, or shipping are highly dependent on the functioning of coastal marine ecosystems [8]. The maintenance and enhancement of these activities as well as of the multiple benefits available from marine ecosystems depend on how societies and governments find ways to balance the demand and the supply of marine ecosystems [9]. Environmental problems

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are very often in the most coastal cities. The importance of active stakeholder participation in management and decision making of protection of the coastal and marine environment has increasingly been acknowledged, and this is now supported and integrated in various recent policies worldwide [3, 10, 11, 12].

The aim of the present study was to investigate resident's perceptions and views about the main sectors that contribute to the development of the city of Kavala and the resident's wellbeing as well as the adequacy of the Stakeholders in their activities for the protection of the coastal and the marine environment.

2. MATERIALS AND METHODS

The research area of this paper was the city of Kavala (350, 61 km^2) in northern Greece, which is the principal seaport of eastern Macedonia and the capital of Kavala regional unit (Figure 1). It is situated on the Bay of Kavala, across from the island of Thasos. The municipality of Kavala also includes the communities of Krinides, Amigdaleonas, Nea Karvali and Zygos with total population 70,501 residents.



Fig. 1 Map of Greece depicting the investigation area

KAVALA OIL S.A, located 18 kilometers south of the city of Kavala is the only hydrocarbon extraction company in Greece from 1978, which produces "crude oil" and "natural gas". Also in Kavala there is a phosphoric fertilizers industry from 1961. The research was carried out with the application of a face to face structured questionnaire which developed for the purpose of this study and consisted of three major parts. The first examined marine and coastal sectors and their contribution to the development and quality life in the city. The second part referred to the factors that mainly pollute the sea (aquatic and terrestrial) and the activities of different Stakeholders. The third part of the questionnaires is about resident's characteristics.

Random sampling was applied. The population ratio that is also the impartial evaluation of the real ratio of the population p and the assessment of the standard error of the population ratio of the

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s_p without correction of the finite population as the sampling fraction is small, has been calculated using the formulae of simple random sampling.

To calculate the size of the sample we thought it would be necessary to conduct pre-sampling with a sample size of 50 individuals. The size of this sample was calculated based on the formulae of simple random sampling (where t = 1.96 and e = 0.048) [13]. Even though simple random sampling without off reset was used, the correction of the finite population can be omitted as the sample size n is small in relation to the population size N [14]. More specifically, the sample size was determined to 400 individuals. The data collection was carried out during the second semester of 2015.

The total of questions which were reported to marine and coastal sectors that contribute to the development of Kavala constitutes a multi-theme variable on which reliability analysis is applied. In particular, in order to find out the internal reliability of a questionnaire [15], i.e. if our data have the tendency to measure the same thing we used the alpha co-efficient (or reliability co-efficient a-Cronbach). If the alpha co-efficient is 0.70 or bigger it is regarded satisfactory [16] and if it is bigger than 0.80 it is regarded very satisfactory. In practice, it is frequent that smaller reliability coefficients, that is with values no bigger than 0.60, are also accepted.

However, the checking must not only be reliable, it must also be credible and this is done through the application of factor analysis [17]. In particular, we used the method of principal components which is based on the spectral analysis of the variance table (correlation). Regarding the significance of the principal components, the criterion which was used was the one suggested by Guttman and Kaiser [15], according to which, the limit for the collection of the appropriate number of the principal components is determined by the values of typical roots which are equal or higher to one. Furthermore, we also used the matrix rotation of the main factors applying the Kaiser's method of maximum variance rotation.

3. RESULTS AND DISCUSSION

3.1. Coastal and marine sectors in the development and the welfare of the city

Coastal and marine areas support economic and social welfare in the adjacent cities [11]. For this reason the coastal area of the city of Kavala constitutes also a comparative advantage for its development and the residents' well-being. To this opinion agree the vast majority (57.8% absolutely and 29.5% very) of the residents of Kavala. Only few (little 1, 8% and 0.3% not at all) have the opposite attitude. 10.8% are indifferent (moderate agree).

Multiple economic activities as fishing, aquaculture, tourism or shipping are highly dependent on the coastal and marine areas and the functioning of the existing ecosystems. [8, 9]. Coastal urban tourism can contribute positively to the social and economic life of a destination [12]. When the residents of Kavala were asked to evaluate different activities contribute to the development of the coast and marine area of the city as most important characterized the touristic development in the coastal zone and the integration of the landscape (Table 1). As important evaluated also the fisheries, the exploitation of under water resources (especially oil extraction) and the attraction of the cruise tourists.

Reliability analysis was applied to the above variables after completing all the necessary checks. The value of the reliability coefficient alpha was 0.846. This is a strong indication that the data tended to measure the same thing. This finding was also supported by the fact that the partial reliability alpha coefficients were significantly higher after the deletion of any variable, and no increase of the reliability coefficient was observed.

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Table1. Residents' evaluation of the marine and coastal sectors to their contribution to the development of Kavala and the resident's well-being.

	Mean	**Std. Deviation**
Fisheries	7.69	1.820
Aquacultures	6.83	2.223
Touristic development of the coastal zone	8.15	1.850
Attraction of cruise tourists	7.46	2.126
Integration of the landscape	7.99	2.027
Fishery as leisure activity	6.69	2.346
Transporting of people	7.05	2.253
Transporting of goods	7.06	2.010
Oil extraction	7.52	2.172
Creation of jobs	7.21	2.580

All the necessary checks were conducted before proceeding with the factor analysis. The value of the Keiser-Meyer-Olkin indicator was 0.865. Furthermore, Bartlett's test of sphericity rejects the null hypothesis that the correction table is unitary and that the partial correlation coefficients are low. The fact that the measures of sampling adequacy have high to very high values also supports the view that the factor analysis model was acceptable. There were three extracted factors. Table 2 lists the load of the partial correlation factors of the ten variables with each of the three factors extracted from the analysis. The higher the load of a variable in a factor, the more this factor is responsible for the total degree of variance of the considered variable.

Table 2. Table with factor burdens after rotation.

variables	**burdens of factors**		
	1	2	3
Fisheries	0.141	**0.795**	0.242
Aquacultures	0.062	**0.735**	0.389
Touristic development of the coastal zone	**0.644**	0.002	0.409
Attraction of cruise tourists	**0.745**	0.099	0.190
Integration of the landscape	**0.734**	0.292	0.032
Fishery as leisure activity	0.522	**0.629**	-0.224
Transporting of people	**0.754**	0.121	0.312
Transporting of goods	**0.569**	0.194	0.465
Oil extraction	0.136	0.234	**0.711**
Creation of jobs	0.332	0.132	**0.708**

The first factor includes the variables "Touristic development of the coastal zone" "Attraction of cruise tourists" Integration of the landscape", "Transporting of people" and "Transporting of goods" referred as comparative advantage of the city for development. The second factor includes the variables "Fisheries", "fishing for leisure" and "aquacultures" and called utilization of the marine resources. Besides the variable "fishery as leisure" with high value 0.522 is a bridge between the first and the second factor. In the third factor the variables of "Oil extraction" and "Creation of jobs" constitute exploit of underwater resources.

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3.2. Factors pollute the sea and the activities of Stakeholders

There are multiple human impacts that threaten the functioning of coastal ecosystems like marine pollution, intensive fishing and oil spills [11]. Asking residents of Kavala to evaluate the factors that pollute the coastal and marine environment, most of them stated that industry waste and pesticides and fertilizers are the main polluters (Table 3). This is reasonableness because of the function of the phosphoric fertilizer industry in Kavala. Also important are rubbishes and plastics and domestic waste. Although there is a hydrocarbon producing company near the city, less important were evaluated according to the residents spot oil and ship accidents and problems created from sediment and soil erosion.

Table 3. Evaluation of the factors pollute the sea.

	Mean	Std. Deviation
Domestic waste	7.53	2.261
Industry waste	8.31	1.970
Pesticides and fertilizers	7.83	1.958
Sediment and erosion of the soil	6.04	2.104
Rubbishes and plastics	7.75	1.875
Ship accidents	6.11	2.674
Spot oil accidents	6.58	2.616

Reliability analysis was applied to the above variables after completing all the necessary checks. The value of the reliability coefficient alpha was 0.827. This is a strong indication that the data tended to measure the same thing. This finding was also supported by the fact that the partial reliability alpha coefficients were significantly higher after the deletion of any variable, and no increase of the reliability coefficient was observed.

Also before factor analysis applied necessary checks conducted. The results from factor analysis are given in Table 4. The first factor includes the terrestrial sources of pollution and the second the marine sources of pollution. As we can see the terrestrial resources evaluated as more important (mean 7.90, s.d. 1.552) than the marine (mean 7.51, s.d. 1.729).

The importance of active stakeholder participation in management and protection of the coastal and marine environment has increasingly been acknowledged and now supported and integrated in various recent policies worldwide [3]. Finally the residents of Kavala were asked to evaluate Stakeholders' activities on the environmental protection and from their response was revealed higher satisfaction for the activities of the ecological and scientific organizations and the residents' community and lower from the State and the Local authorities (Table 5).

Table 4. Table with factor burdens after rotation.

Variables	burdens of factors	
	1	2
Domestic waste	**0.827**	0.014
Industry waste	**0.819**	0.178
Pesticides and fertilizers	**0.709**	0.322
Sediment and erosion of the soil	**0.565**	0.372
Rubbishes and plastics	**0.577**	0.331
Ship accidents	0.225	**0.889**
Spot oil accidents	0.190	**0.908**

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Table 5. Evaluation of the Stakeholder's activities to the protection of the coastal and marine environment.

Stakeholder	Very much Satisfied	Very Satisfied	Satisfied	Little Satisfied	Not at all Satisfied	No answer
Local authority	2.3%	6.8%	28.3%	44.5%	18.3%	
Regional authority	1.8%	6.0%	25.5%	46.8%	19.8%	0.3%
State	0.5%	5.5%	17.0%	46.0%	30.5%	0,5%
Scientific	1.5%	6.8%	43.0%	37.5%	11.0%	0,3%
Ecological NGO	1.3%	14.5%	40.3%	35.0%	8.5%	0,5%
Local media	0.5%	5.3%	32.5%	45.0%	16.3%	0.5%
Port authorities	0.8%	7.5%	37.0%	41.8%	13.0%	
Kavala Port Org.	1.3%	6.5%	35.3%	42.5%	14.3%	0.3%

3.3 Demographic profile of the respondents

During the interviews, the residents were also asked about their demographic profile. As shown in Table 6 55.6% of the respondents questioned were male and 44% were female. Most of them (33.8%) were middle aged (30-40 years), married (56.5%). As regards their profession, they were mainly (28.8%) public servants or private employee (23.1%) Their educational level was high, since over 31.1% of the respondents had completed university or technological education (28.8%).

Table 6. Socio-demographic profile of the sample %

Gender	Male	Female		
	55.6%	44.4%		
Age	18-30	31-40	41-50	> 50
	24.8%	33.8%	27.5%	14%
Marital Status	unmarried	Married	divorced or widowed	
	39.5%	56.5%	4.5%	
Educational Level	Primary School	Lower Secondary	Technical School	
	0.8%	5.3%	7.5%	
	Upper Secondary	Technological ed.	University	
	26.6%	28.8%	31.1%	
Profession	private employee	public servants	self-employed	
	23.1%	28.8%	12.8%	4%
	pensioners	Students	housewives	Unemployed
	5.5%	7.8%	5.3%	12.5%

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4. CONCLUSIONS

Sustainable cities must be planned with respect to environmental quality and to be simultaneously economically viable, socially just, politically well managed to maximize and human well-being [19]. The coastal and marine environment constitute a great advantage to the city of Kavala and consequently residents evaluated the coastal zone tourist development and landscape integration as highly important for the city development and residents wellbeing. For this reason, it is absolutely necessary for residents and Stakeholders to protect this area from risk of pollution from hydrocarbon production and the phosphoric fertilizers industry. Residents considered the industrial waste, pesticides and fertilizers as major pollutants of the marine environment so the Stakeholders have to be more careful in industry controls. Besides that, residents were alert in sea pollution symptoms and worried for the worst case scenario in planning for potential disasters. The importance of active stakeholder participation in management and decision making of protection of the coastal and marine environment has to be been integrated in various recent policies because residents were not satisfied from the activities of the government stakeholders. Less rigorous were with the others stakeholders active in environmental protection.

References

[1] Kuleli T., 2015. The socio-economic significance of the Turkish coastal environment for sustainable development. *Environmental Monitoring and Assessment* **187**, 231.

[2] Nicholls, R.J., Hanson, S., Herweijer C., Patmore, N., Hallegatte, S., Jan Corfee-Mortot, Jean Chateau, Muir-Wood, R., 2007. Ranking of the word's cities most exposed to coastal flooding today and in the future. *OECD, Environment Working Paper* No 1.

[3] Marre, J.B., Pascoe, S., Thebaud, O., Jennings, S., Boncoeur, J., Coglan, L., 2016. Information preferences for the evaluation of coastal development impacts on ecosystem services: A multi-criteria assessment in the Australian context. *Journal of Environmental Management* **173,** 141-150.

[4] Papamanolis N., 2015. The main characteristics of the urban climate and air quality in Greece cities. *Urban Climate* **12,** 49-54.

[5] De Groot, R., Brander, L., Costanza, R., Bernard, F.,.Braat, L., Christie, N., Crossman, M., Ghermandi, A.,.Hein, L., Hussain, S.,.Kumar, P., A.McVittie, A., Portela, R., Rodriguez, L., , Ten Brink, C., Van Beukering, P., 2012. Global estimates of the value of ecosystems and their services in monetary units, *Ecosystem Services* **1,** 51-60.

[6] Folke, C.,Jansson, A., Rockström, J., Olsson, P..Carpenter, S.R , Chapin F.S., Crèpin, A.S., Daily, G., Danell, K., Ebbesson, J., Elmqvist, T., Galaz, V., Moberg, F., Nilsson M., Österblom, H., Ostrom, E.,.Persson, Å., Peterson, G., Polasky, S., Steffen, W., Walker, B., Westley, F., 2011. Reconnecting to the biosphere, *AMBIO* **40,** 719-738.

[7] Vitousek, P.M. Mooney, H.A., Lubchenco, J., Melillo, J.M., 1997. Human domination of Earth's ecosystems. *Science* **277,** 494-499.

[8] Outeriro, L., Villasante, S., 2013. Linking salmon aquaculture synergies and trade-offs on ecosystem services to human wellbeing constituents. *AMBIO* **42**, 1022–1036.

[9] Costanza, R., deGroot, R., Sulton, P., Vander-Ploeg S., Anderson, S.J., Kubiszewski, I., Farber S., Turner, R. K., 2014. Changes in the global value of ecosystem services, *Global Environmental Changes* **26**, 152–158.

[10] Reed, M.S., 2008. Stakeholder participation for environmental management: a literature review. *Biological Conservation,* **141**, 2417-2431.

[11] Rivero, S., Villasante, S., 2016. What are the research priorities for marine ecosystem services? *Marine Policy,* **66,** 104-113.

[12] Carlisle, S., Johansen, A., Kunc, M., 2016. Strategic foresight for (coastal) urban tourism market complexity: The case of Bournemouth. *Tourism Management,* **54,** 81-95.

[13] Matis K. G., 2001. Forest Sampling, University of Thessaloniki, Thessaloniki.

[14] Pagano, M., Gauvreau, K., 2000. Principles of Biostatistics, Ellin Publications.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[15] Frangos, X. K., 2004. Market Research Methodology and Data Analysis with the application of the Statistical Package SPSS FOR WINDOWS, Interbooks Publications.
[16] Howitt, D., Gramer, D., 2003. *Statistics with SPSS 11 and Windows,* Klidarithmos, Athens.
[17] Tabachick, B. G., Fidell, L. S., 1989. *Using Multivariete Statistics.* Harper and Row, New York.
[18] Harman, H. H., 1976. *Modern Factor Analysis.* The University of Chicago Press, Chicago.
[19] Panagopoulos, T., González Duque, J.A., Dan, M.B. 2016. Urban planning with respect to environmental quality and human well-being. *Environmental Pollution*, **208**, 137-144, http://dx.doi.org/10.1016/j.envpol.2015.07.038

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Towards a Zero Energy Demand Building: Recent data of the experimental prototype unit ZED-KIM

P. Kosmopoulos*, P. Touboulidis, A. Moumtzakis, A. Kantzioura

Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements,
Democritus University of Thrace, 67100, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

Aiming at the energy efficiency of the building sector through the adoption of near Zero Energy Buildings, the project of the Experimental Prototype Unit ZED-KIM applies new technologies of Renewable Energy Sources and methods of Energy Saving.

This paper presents and describes the autonomous (off-grid) experimental house ZED-KIM (Zero Energy Demand - Kimmeria), located at the Campus of the Engineering School, DUTH at Xanthi, in Kimmeria.

The aim of this project is to study the possibility of installing Renewable Energy Sources systems for power sufficiency. In the pilot house there is a hybrid system of photovoltaics and a wind generator. The system is connected to a monitoring system for continuous and advanced recording of the energy production in order to be possible the collection and the analysis of the experimental data. Also, a solar air collector heater is installed in order to minimize the energy demands for heating and to investigate its contribution in energy saving. In order to achieve useful and helpful data, a full year's results in energy production by RES (Jun 2015-Jun 2016) are presented and analyzed.

ZED-KIM leads us to consume that even in Northern Greece housing units can be at least near zero energy buildings, regarding electricity demands of a mean household.

Keywords: ZEB; RES; off-grid; hybrid systems; energy production

1. INTRODUCTION

Renewable energy continued to grow against the backdrop of increasing global energy consumption, particularly in developing countries. Globally, there is growing awareness that increased deployment of renewable energy (and energy efficiency) is critical for addressing climate change, creating new economic opportunities, and providing energy access to the billions of people still living without modern energy services. So, renewable energy provided an estimated 19.1% of global final energy consumption in 2013, and growth in capacity and generation continued to expand [1].

According to the Renewable Energy Statistics [2], there was a particularly rapid expansion in the output of wind and solar energy, which accounted for 10.5 % and 5.5 % respectively of the EU-28's renewable energy produced in 2013.

At the same time while energy requirements are increasing continually due to technological development and the overpopulation of the planet, there is a concern over the adequacy of energy sources and the rising of the cost of energy, which play a catalytic role in the economic crisis which permeates the world community at the present time (world financial crisis). Over the last years prices of oil, natural gas and uranium have almost tripled [3], while the cost of carbon dioxide emissions has increased almost by 25% [4].

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Also, the EU Members adopt national action plans in order to achieve the target of 20-20-20 until 2020, so as to achieve 20% more use of RES in comparison to 1990.

According to the Directive 2010/31/EU, Energy Performance of Buildings Directive (EPBD), all new buildings in EU member states must be nearly-Zero Energy Buildings (nZEBs) by 2020 (for buildings occupied or owned by public authorities by 2018). Also, all EU member states shall draw up national plans such as retrofitting existing buildings to increase the number of nZEBs [5].
Finally, the regulation about net-metering in Greece has launched the photovoltaic systems (PV) in building sector, in order to cover the energy needs from RES.

In this direction, the present study describes and analyzes data from the autonomous experimental house ZED-KIM (Zero Energy Demand). ZED-KIM has been developed at the Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements. The aforementioned house is located in the region of Kimmeria, 4 kilometers east of the town of Xanthi.

The aim of this research effort is the practical efficiency of R.E.S. systems and more specifically that of photovoltaic and wind generators as well as their contribution to the coverage of energy demands which may be attained by the installment of similar provisions in a mean household in Northern Greece, together with the prevailing climatic conditions and seasonal fluctuations throughout the year.

2. METHODOLOGY: DESCRIPTION OF ZED-KIM (ZERO ENERGY DEMANDS - KIMMERIA)

The prefabricated experimental house ZED-KIM, which consists of an imitation of an average household on a scale of 1:5, the general image of which is presented in picture 1, has been constructed in such a way so as to conform to bioclimatic design principles [6]. Its ground plan is rectangular and 20 m^2 in total, the house faces south with an azimuth angle of 0^o. It has two windows, one on the south and one on the east side, which allow sun light to enter, thus increasing thermal energy. On the south and west sides (the most significant winds) evergreen trees have been planted for shade in the summer and protection in winter. At this point it is worth mentioning that this pilot house is very well insulated, its roof provides additional thermal insulation and sound proofing [7]. The roof is tilted at 42^o which is considered the most appropriate slant for the latitude of the city of Xanthi, in order to exploit the greatest levels and intensity of solar radiation during the sunny months [8,9]. Six photovoltaic panels of multi- crystalline silicon (total area 6,4 m^2 and 1020 W) have been installed on the roof [10].

According to the climatic and techno-economic studies which were carried out in the region of Kimmeria, aiming at installing an ideal R.E.S. system for the area in order to cover the energy requirements of the application, which will exploit harmoniously both the solar and wind power of the area, an autonomous photovoltaic hybrid system which is also linked to the PPC Grid to line was installed. The whole system is a pilot one as its functioning may be either autonomous or connected to the central grid. More specifically, when the total stores from the renewable energy sources (R.E.S.) are insufficient to cover the needs of the household, then they are covered by the central network. On the other hand, when there is a surplus (which happens most of the time) this is fed into the central grid.

Besides the photovoltaic array (1020W) as was mentioned before, another photovoltaic panel is installed with a two axis tracker (1100watt) with the potential of autonomous and off – feeding electrical rotation 120^o in the direction of east – west every 20 minutes. This rotation is determined by a solar monitor (Figure 2).

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Figure 2. The prefabricated house ZED-KIM.



Figure 3. PV array with a two axis tracker (1100W)



Figure 4. Wind turbine (900W)

The afore-mentioned array consists of two photovoltaic panels of multi-crystalline silicon and two of mono-crystalline silicon, each of the same power. Each of these systems and their different technologies are compared through experimental investigation of their thermal and electric characteristics. On the west side of the house a wind generator has been installed, which has been carefully studied in order to function alongside the hybrid system in connection with the photovoltaic modules and to help considerably in the production of energy during seasonal fluctuations (wattage 900watt with wind speed rotation 2.7 m/s) (Figure 3).

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The total production of the installed R.E.S. (3kW) contributes to a complete system, consisting of 3 inverters (DC/AC), 1 charge controller linked to a storage cell system (200Ah – 12V) and 1 control unit which records data which communicate with the computer.

Finally, it is worth noting that in the ZED-KIM a complete system has been installed to follow and record meteorological conditions, which can be seen on the left and right side of the house (Figure 1). This system consists of a wind cup anemometer, rain gauge, temperature and humidity gauge, barometer, two pyranometers to measure total solar radiation and one pyranometer with a shadow ring to measure the intensity of diffuse solar radiation.

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Figure 5. Recording and storage cell system

3. RESULTS AND DISCUSSION

According to the data collected, which are the results of yearly measurements, Table 1 presents an analytical monthly and yearly production of energy, a total figure and a figure for each renewable source of energy installed in the ZED-KIM house.

Table 1. Monthly and yearly production of electrical energy

	Rotating PV (kWh)	Steady PV (kWh)	Total PV (kWh)	W/G (kWh)	Total (kWh)
Jan	79.03	70.63	149.66	67.02	216.68
Feb	77.03	88.54	165.57	77.80	243.37
Mar	94.30	80.56	174.86	110.82	285.68
Apr	144.09	117.79	261.88	31.58	293.46
May	171.42	130.44	301.86	28.71	330.57
Jun	154.81	111.82	266.63	96.41	363.04
Jul	201.12	147.04	348.16	60.42	408.58
Aug	191.11	153.20	344.30	98.99	443.29
Sep	143.47	123.91	267.38	89.73	357.11
Oct	111.49	100.36	211.85	124.20	336.05
Nov	105.59	100.75	206.34	36.90	243.24
Dec	96.00	104.97	200.98	70.58	271.55
Total (kWh/year)	**1569.44**	**1330.03**	**2899.47**	**893.15**	**3792.61**

The total electrical energy which is collected and used by the system yearly is in the range of 3793 kWh, within which the rotating two axis photovoltaic tracker produces 1570 kWh, the photovoltaic array on the roof produces 1330 kWh while the wind generator produces 893 kWh.

In Figure 5 there is an association of the total produced energy of the system per month, with the corresponding total of the photovoltaics and wind generator.

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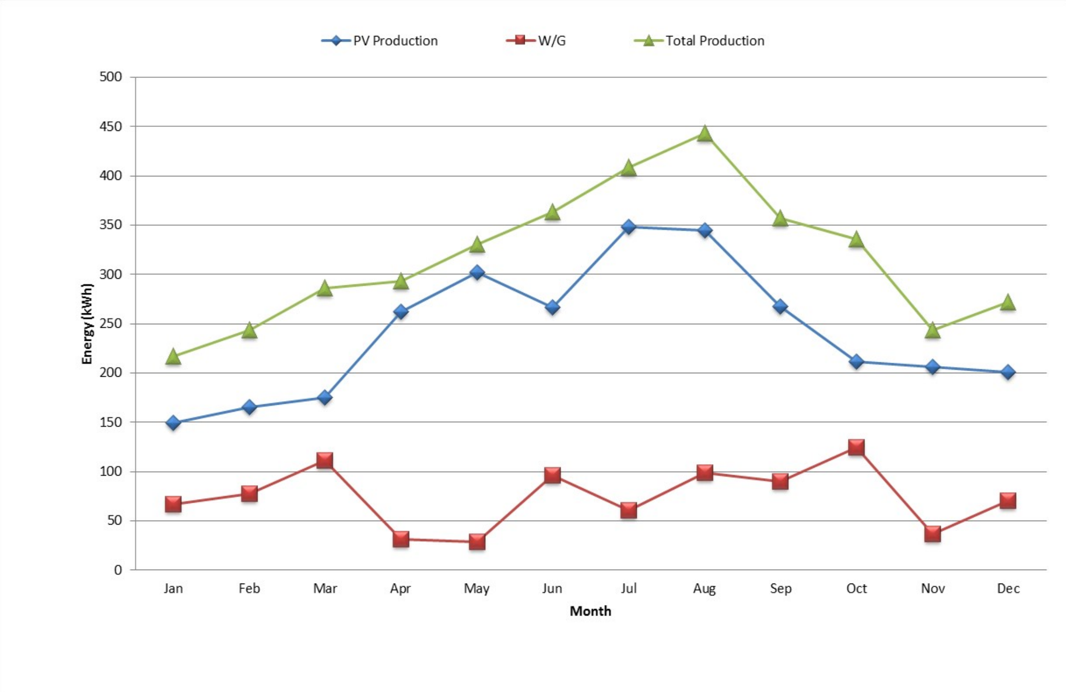


Figure 6. Monthly production of electrical energy 2015

In Figure 6 the total electrical energy from the installed R.E.S. is presented per month.

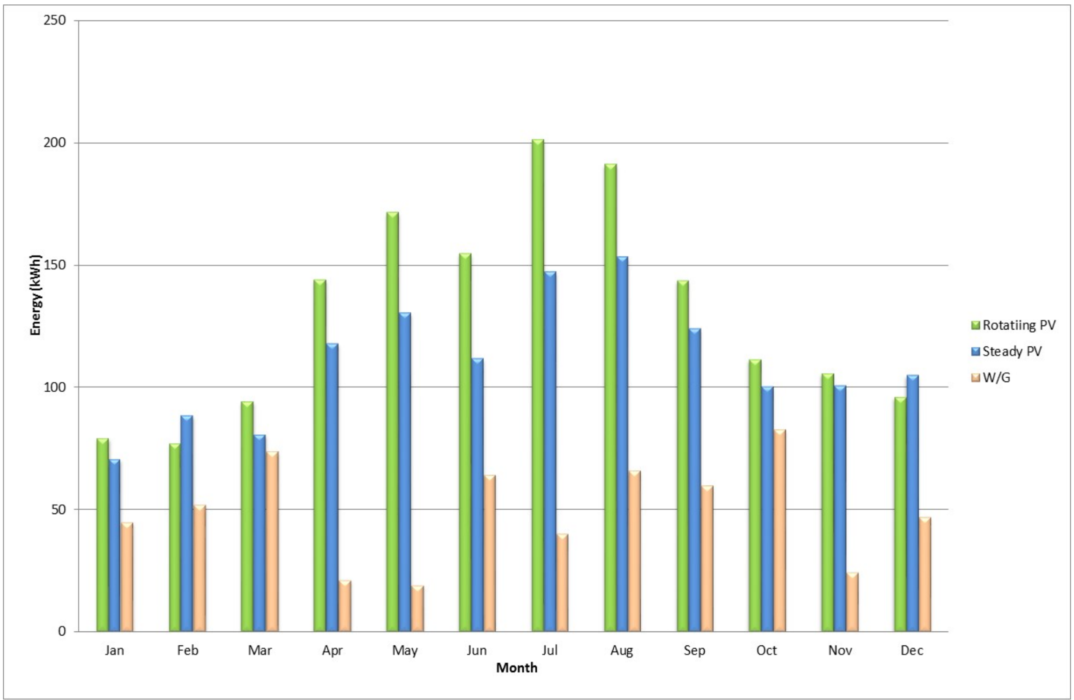


Figure 7. Monthly production of electrical energy of each R.E.S.

As presented in Table 2 which follows, the minimum total energy produced by the system per day ranges between 7.3 to 9.5 kWh during the winter, while the largest amount ever recorded reaches 14.3 kWh during days with a high level of solar radiation and strong winds.

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In Table 3 which follows, the percentages of total energy as well as the energy produced by

Month	Rotating PV (1kW) (kWh)	Steady PV (1kW) (kWh)	PV production (kWh)	W/G (kWh)	Total production (kWh)
January	2.5	2.4	4.9	2.4	7.3
February	3.6	3.5	7.1	2.4	9.5
March	3.3	2.8	6.1	3.75	9.85
April	5.0	4.2	9.2	0.75	9.95
May	5.5	4.2	9.7	0.9	10.6
June	5.2	3.7	8.9	3.15	12.05
July	6.0	4.5	10.5	1.95	12.45
August	6.2	4.9	11.1	3.15	14.25
September	4.8	4.1	8.9	3.0	11.9
October	3.6	3.2	6.8	4.05	10.85
November	3.5	3.4	6.9	1.2	8.1
December	3.2	2.9	6.1	2.1	8.2

each installed R.E.S. system in the ZED-KIM house, are presented on a monthly and yearly basis.

Table 2. Daily produced electrical energy

Table 3. Percentage of produced electrical energy 2015

Month	Rotating PV	Steady PV	Total PV	W/G
Jan	36.5%	32.6%	69.1%	30.9%
Feb	31.6%	36.4%	68.0%	32.0%
Mar	33.0%	28.2%	61.2%	38.8%
Apr	49.1%	40.1%	89.2%	10.8%
May	51.9%	39.5%	91.3%	8.7%
Jun	42.6%	30.8%	73.4%	26.6%
Jul	49.2%	36.0%	85.2%	14.8%
Aug	43.1%	34.6%	77.7%	22.3%
Sep	40.2%	34.7%	74.9%	25.1%
Oct	33.2%	29.9%	63.0%	37.0%
Nov	43.4%	41.4%	84.8%	15.2%
Dec	35.4%	38.7%	74.0%	26.0%
Total (kWh/year)	**41.4%**	**35.1%**	**76.5%**	**23.5%**

Of the total electrical production approximately 76.5% stems from the installed photovoltaic systems (41.4% rotating PV, 35% steady PV) while 23.5% is from the wind generator. During the winter period when it is very cloudy or when there are strong winds, the contribution to the production of electrical energy made by the photovoltaics is reduced to 30%**.** A significant merit of electrical energy during this period, comes from the wind generator (32%). During the summer, however, the aforementioned situation is more intense, and the photovoltaics produce 91% of the

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energy, limiting the contribution of the wind generator to an amount of 9%. The above results are presented in Figure 7.

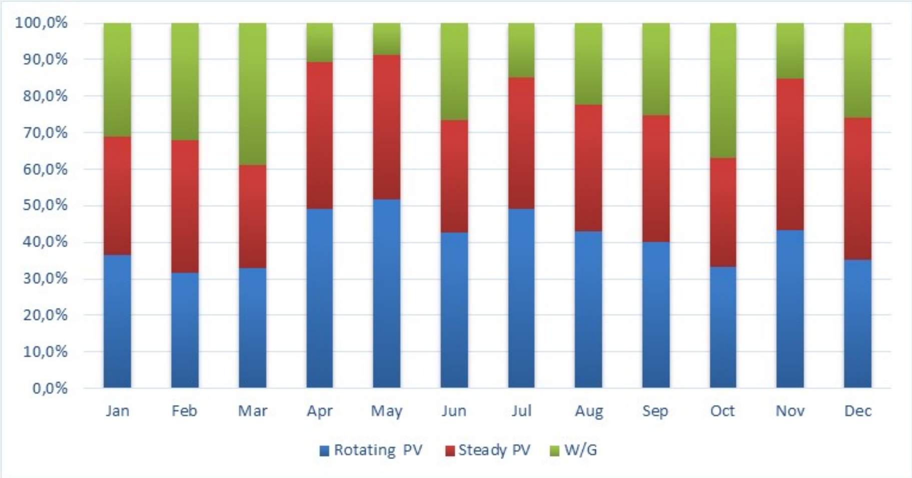


Figure 8. Percentage production of electrical energy from each R.E.S.

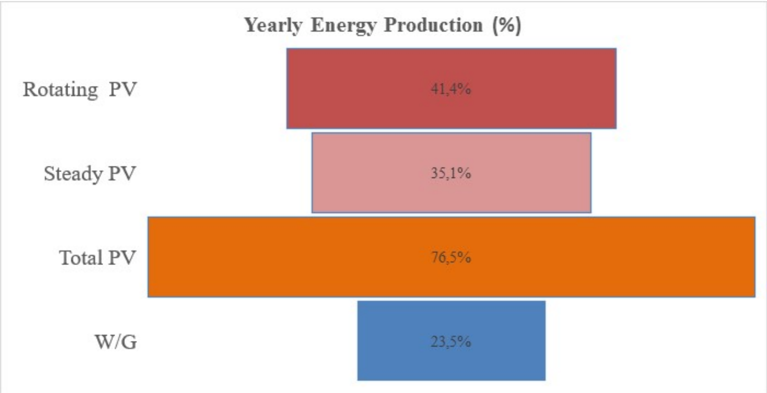


Figure 9. Percentage of yearly energy production from each RES

At this point, it is worth mentioning and analyzing the difference in the levels of electrical production of the rotating and fixed photovoltaic arrays. During the summer months when the two systems are exposed to high levels of solar energy, a dominance of the rotating PV array is noted, against the amount of the fixed PV array (25%) which corresponds to about 45kWh a month production of electrical energy [10,11]. The above phenomenon is noted in a smaller scale during low levels of solar radiation (the winter period). This is due to the fact that the produced wattage from each photovoltaic cell, depends significantly on the produced intense of electrical current which relates directly to solar radiation. In contrast, voltage increases with the slightest exposure to low level solar radiation [12]. Thus, due to the fact that during the winter months diffuse solar radiation dominates to a great extent, which falls upon the two photovoltaic systems at the same level independent of the azimuth angle from the south, it has been noted that the percentage of energy production between the rotating PV array and the steady PV array installed in the ZED-KIM is smaller than in the summer period (25%).

4. CONCLUSIONS

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According to the data presented in this research it can be stated that if the results of the pilot house (scale 1:5) are transferred into reality and photovoltaic arrays 5 times more (~10kW) and wind generator of 1.5 times more (~1.5 kW), the power are installed, with a yearly total production of 3793 kWh the following will occur: In an average household of 4-5 people with a house of 100 m^2 and appropriate insulation, in difficult climatic conditions such as in Northern Greece, 15837kWh of energy are expected to be produced yearly. This will exceed the needs of an average household and the surplus energy may be sold back to the PPC (0.11 €/kWh). From the above it can be easily acknowledgment that for the covering of the aforementioned needs 5000 kWh yearly are required, a system's payback period is of 10 years, with today's market prices and no tax-free purchase, with considerable reduction in the forthcoming years as R.E.S. technology develops and improves. In figure 8 which follows, the cumulative cash flows and the payback period are presented in a 30-year basis.

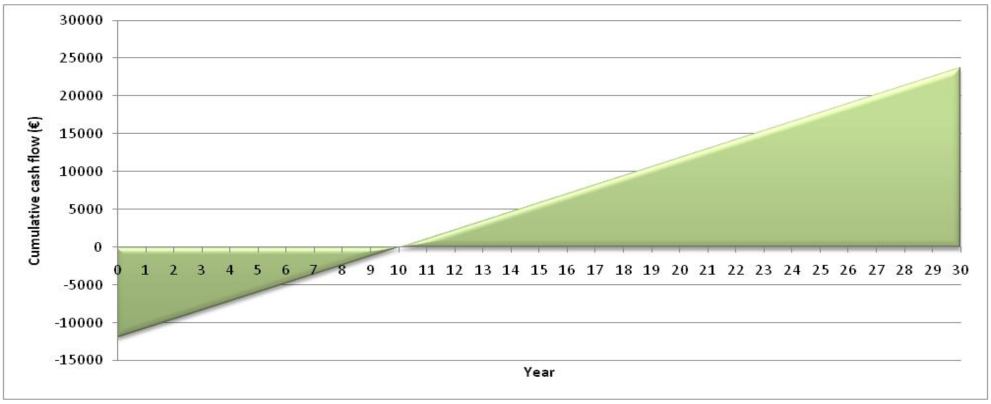


Figure 8. Cumulative cash flows graph

Furthermore, it has been shown that the city of Xanthi which is located in Northern Greece, has high solar and wind potential which makes it suitable for the installation of hybrid systems. These systems can exploit the north-eastern Greece wind and solar potential towards satisfactory electrical production throughout the unstable weather patterns yearly.

Finally, it has been proved that photovoltaic arrays in two axis tracker, increase the yearly electrical production by 27% compared to those that are placed at a steady angle, equal to the latitude of the place. This percentage exceeds 25% during the summer months.

References

[1] REN21, *Renewable Energy Policy Network for the 21st century, Renewables 2015 Global Status Report, Annual Reporting on Renewables: Ten years of excellence*, 2015

[2] Eurostat statistics explained, May 2015

[3] International Energy Agency. http://www.iea.org/, Visit online at 08-7-2014.

[4] Zerefos, C. 2008. *Prologue, in "Buildings, Energy and the Environment, 1st Edition"* (Kosmopoulos P., ed). University Studio Press, Thessaloniki

[5] Directive 2010/31/EU of the European Parliament and of the Council of 19 May 2010 on the energy performance of buildings. Published in Official Journal of the European Union.

[6] Kosmopoulos, P. and D. Galanos. 2006. *The use of renewable energy source in houses (ZED-KIM)*. The 3rd Conference on Passive and Low Energy Architecture. Geneva, Switzerland, 6-8 September

[7] Papadopoulos, A. 2000. *Feasibility of energy saving measures in multi-use building'. Congress on heating, refrigerating and air-conditioning*. Belgrade, Pages 233-241.

[8] Hussein, H.M.S., Ahmad, G.E. and H.H. El-Ghetany 2004 *Performance evaluation of photovoltaic modules at different tilt angles and orientations.* Energy Conversion and Management, 45: 2441–2452

[9] Kosmopoulos, P. 2000. *Environmental Psychology*. University Studio Press, Thessaloniki

ISBN: 978-960-6865-94-7

[10] Kosmopoulos, P. 2008. *Less energy demand, less emissions*, in ‘Buildings, Energy and the Environment, 1st Edition’ (Kosmopoulos P., ed). University Studio Press, Thessaloniki.
[11] Centre for Renewable Energy Sources and Saving. http://www.cres.gr/. Visit online at 12-7-2014.
[12] Kalapodas Ch. 2011. *Experimental Research of Energy Efficiency in PV and W/G systems in the house ZED-KIM, D.U.TH.*, Xanthi, Greece
[13] Nikou, A. 2010. *Research of the Energy Efficiency of the House ZED-KIM for Buildings and Settlements Design*. D.U.TH., Xanthi

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Rapid development of sustainable housing for disaster relief

P. Kosmopoulos*, E. Alexopoulou

Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements,
Democritus University of Thrace, 67100, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

In response to pressing housing issues arising due to the current refugee crisis we examine sustainable pre-fabricated housing solutions, developed in Greece during the past few years. Individual issues addressed include the prefabrication process in relation to the psychological state of the residents to be, a sustainable approach to the design and fabrication process and the energy needs of the housing units in correlation with providing comfort conditions for the inhabitants. In any case, the aim of a pre-fabricated unit, as we are describing it in this paper, is to be an example of bioclimatic human-oriented design.

Keywords: disaster relief; prefabrication; mass customization; sustainability; housing units

1. INTRODUCTION

The current refugee crisis is a major issue related to both socio-cultural and environmental issues. The relocation of large populations raises –among others- pressing housing issues. In this paper we attempt to face the complex problems arising by proposing sustainable pre-fabricated housing solutions for the affected. Main area of interest is the Mediterranean basin, specifically the eastern region of it, as a place carrying the burden of the refugee crisis. The prevailing climate and vernacular architectural are taken into account, as well as the varying and even conflicting lifestyle of the residents of the area and the residents to be.

Simultaneously, energy needs worldwide are growing rapidly, as the building sector continuous to grow without taking into account the energy consumed throughout the life cycle of a building. According to evidence, the rate of energy consumption in buildings is estimated at 47 % globally. [1] In our days, it is obvious that there is need for eco -friendly building, due to the increasing environmental degradation. Concerns on the subject include the reduction of environmental problems arising both during construction and operation of buildings, addressing mainly the issue of reduction of energy consumption. The aforementioned, plus the interest on natural building, low cost construction and maintenance of buildings have been strong incentives to conduct this study.

A prefabricated unit, has specific requirements, varying from those of a permanent structure, such as portability, low weight and –in most cases- low cost. The reference to the house with the word "unit" is deliberate, because it is perceived as the product of an industrialized process (prefabrication) and not as a unique architectural creation. The aim of this paper is to present some projects regarding prefabricated eco-housing units, based on several projects, developed in Greece during the past years. Issues raised, address three main topics of interest, a) the very idea of prefabrication in relation to the comfort needs of the inhabitants, b) embodied energy of the housing unit, meaning a sustainable approach of all stages of design and fabrication and c) autonomous operation of the unit, concerning its energy needs, along with providing comfort conditions for the inhabitants.

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2. MATERIALS AND METHODS

As aforementioned there are three main topics investigated in the present paper. The process following includes the approach to each through the presentation of an individual paradigm of pre-fabricated housing unit and the process of its design and evaluation. Main aim is to sum up all the elements and qualities needed for an integrated design process to achieve the best possible solution for the problem of sustainable emergency housing.

The first issue is related to the very idea of prefabricated dwellings in relation to the struggle of providing comfort conditions to the inhabitants. This issue can be addressed by facing the design process with a focus on human needs. The main target-group of pre-fabricated housing units is people of low income or victims of –natural and manmade- disasters. The goal is to design a cheap and easily prefabricated and assembled unit that can meet the housing needs of any inhabitant, from a single person to an extended family. As a consequence, placing special emphasis on methodology is vital in order to ensure the possibility of appropriation of space.

The issue of ensuring a low amount of embodied energy in the final housing unit can be addressed through the choice of materials and fabrication techniques, along with the process of on-site assembly. Eco-friendly and recyclable and/or recycled materials can be used on the making of the unit. With a proper organization of the fabrication process, material waste and energy needs can be minimized. Additionally, provision concerning the transportation of the unit components is essential, as the fabrication and the assembly place can be miles away from each other. As for the assembly procedure, it must be as simple as possible, with a minimum use of effort and extras, such as adhesives and coatings. In the case of using extra materials, the design can encourage the use of those available locally, ideally on site. The issue of autonomous operation can be addressed through the consideration, during the design process, of the climate of the area where the unit should be installed and also the proper choice of materials, passive and active systems.

It is vividly clear that taking into consideration the local climate conditions of the area in which the housing unit is going to be installed, along with the proper choice of building materials and passive –and active- systems, is crucial for the comfort conditions provided in relation to the energy consumption. In other words, thermal comfort in any climate should be provided to the inhabitants with the help of thermal mass and the use of sun to raise the air temperature and ventilation to reduce it. Electricity needs can be –in most cases- easily provided by renewable energy sources, such as wind turbines and solar panels. Managing the water is another key issue, on the autonomous function of the housing unit

3. RESULTS AND DISCUSSION

An emergency housing unit should be the reintegration tool in social life. Consequently, the new residence should meet one’s individual needs as the first step to restore the routine. The participatory process of creating the house, through the completion of questionnaires, increases creativity and removes the sense of temporary. In any case, the goal of a pre-fabricated unit, as we are describing it on this paper, is to establish principles concerning respect for the environment and the landscape, man and nature, the reduction of energy consumption and sustainability in general.

3.1 Mass customization

The project presented in this paper, which demonstrates a deep human-focused approach, is entitled “Emergency management in the area of Mediterranean Sea. Mass customization in disaster relief sheltering through activity based design”, a diploma thesis by Alexopoulou Efstratia and Roupa Eleni at the Technical University of Crete, Faculty of Architecture, completed in 2012 with the supervision of Dr. Oungrinis and Dr. Giannoudis. [2] In this approach there was no focus on solving

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technical issues or estimating financial data, issues which undoubtedly have increased importance in the field of emergency housing. The main concern was the quality of the habitation space itself, in the terms of quick and easy appropriation of the space, focusing on the customization of the prototypes, thus challenging the idea of a prefabricated house as a compact unit. Through the process formed, the future user of the house is given the opportunity to select the spaces to compose their new residence. The union of these space vessels leads to the assembly of the residence, which is unique and claims to fulfil the individual needs of each user.

The questionnaires, which form the main part of the process of individuation of housing, are divided in four groups according to the age of the person filling (children, teenagers, adults and elderly). Through questionnaires, the people asked are given the opportunity to choose activities that they used to have in their former area of habitation or would like to have and the kind of space they prefer for those activities. They are also asked to fill an estimated daily schedule, i.e. to record a typical day. Based on the four-group division (according to age) the activities carried out in a house are examined and related to qualities such as posture, tension, etc., as shown in Figure 1. Then, based on the above, activities are mapped to spatial qualities as section sketches, which again vary by age group. Finally a pivot table of sketches of individual spaces is created.

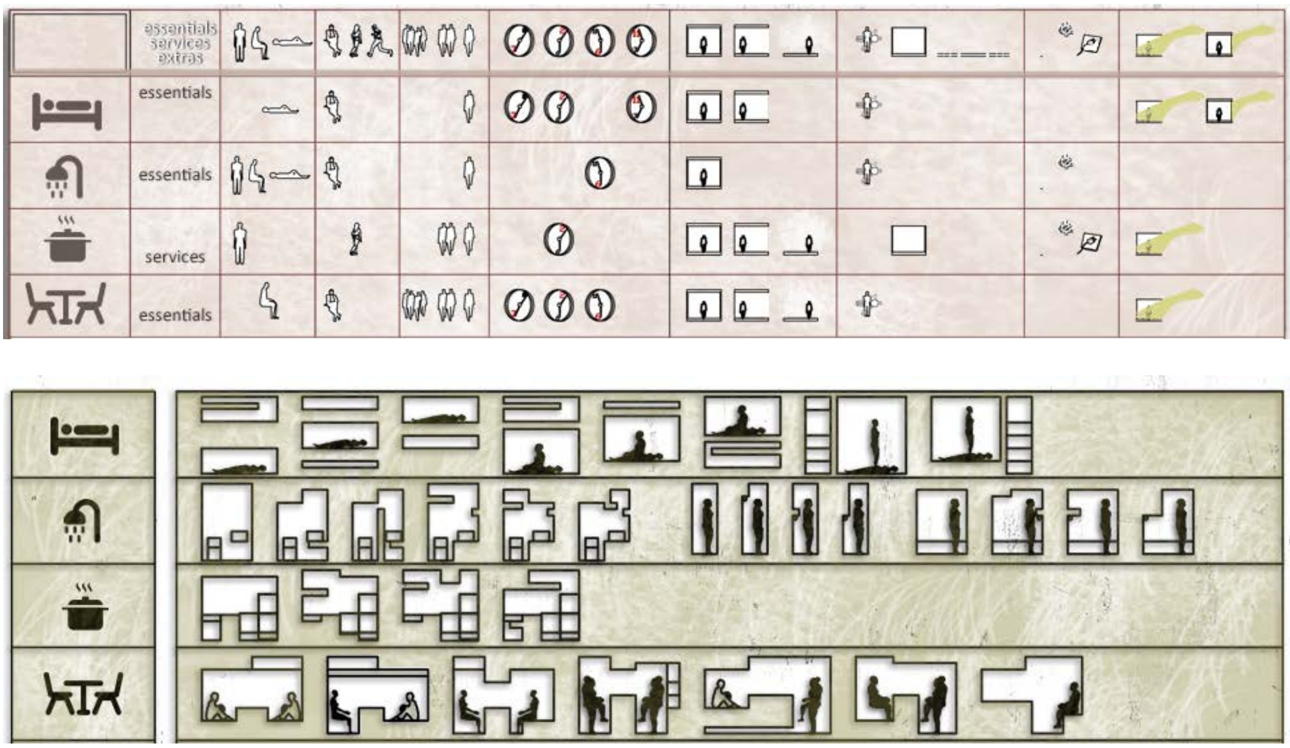


Figure 1. Above: Sample of the table referring to adolescents, displaying the relation between activities and space qualities. Bellow: Sample of the pivot table combining activities and spatial sections. [2]

On the third phase of the project, some habitation scenarios are formed, in order to demonstrate the process required -beginning from the questionnaire- to customize the housing unit to be formed. The scenarios are diverse enough to present the capability of customization, the individuality of each unit. One of the scenarios is presented on a more detailed scale to demonstrate some of the technical issues addressed and the choice of materials. Parts of this illustrated process can be seen in Figure 2.

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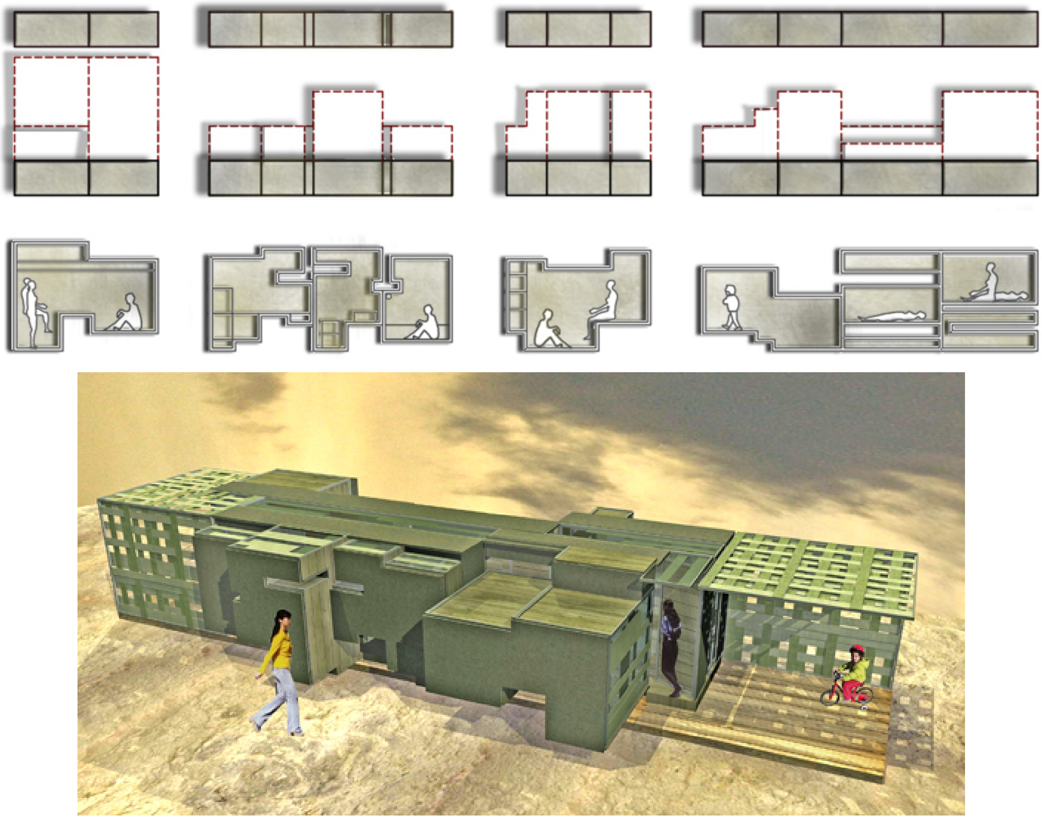


Figure 2. A habitation scenario and a 3d model of a housing unit. [2]

3.2 Sustainable approach to design and energy self-efficiency

Investigating the sustainability of a prefabricated dwelling both during its manufacturing /assembly and operation phases, we base our arguments on a study first begun in 1974 by Dr. Kosmopoulos P. [3] concerning a prefabricated modular housing unit, and its variations over the years. I.e. in 2007 Dimitris Voutsas [4] worked further on the project in the framework of his diploma thesis with the supervision of Dr. Kosmopoulos P., adjusting it to the modern needs, utilizing environmentally friendly materials and building /fabrication techniques. In 2011 Andri Achilleos [5] emphasized on the environmental assessment of the unit, comparing its performance in varying climates. The key objectives set for the design of the unit are: a) use of recyclable, environmentally friendly materials, b) a comfortable temperature in any climate, c) generating electricity by using renewable energy sources and d) collecting rainwater.

The design of the units is based on the principles of bioclimatic design and the principles underlying prefabrication, such as the capability to be easily transferred and the low weight of the whole structure, also there are a finite number of prefabricated elements that can be combined to synthesize diverse types of units. The prefabricated components of the unit, as shown in Figure 3, are made at the factory, but assembled on site. Thus, the modules can be easily transported in the field by truck, ship or helicopter due to low weight and volume.

The housing unit consists of two modular types demonstrated in Figure 4. Module 1 has a free plan, while module 2 acts as a binding unit, giving freedom of choice in the configuration of the partitions. Module 2 also has the ability to operate also as a small patio given roof openings. The dividing walls between units are Trombe walls with lockers, to accumulate thermal mass thus exploiting solar radiation by the small patio and conservatory, which thanks to vents, allow air circulation among spaces. The bathroom is a separate unit with integrated hydraulic and electrical systems and external sockets for connection, and so is the kitchen. The whole structure is mounted

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on a metal steel frame elevated from the ground. In the Figures 5 a typical plan and section of a unit formation i presented.

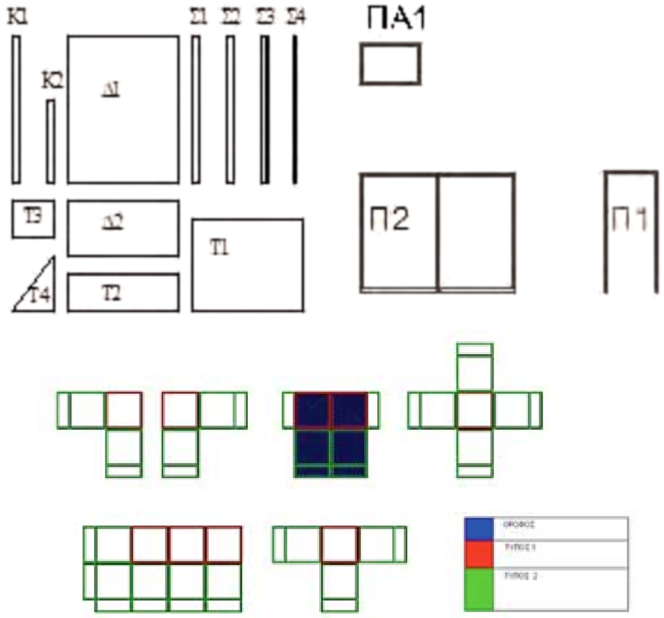


Figure 3. Prefabricated components and variety of forms that can be achieved. [5]

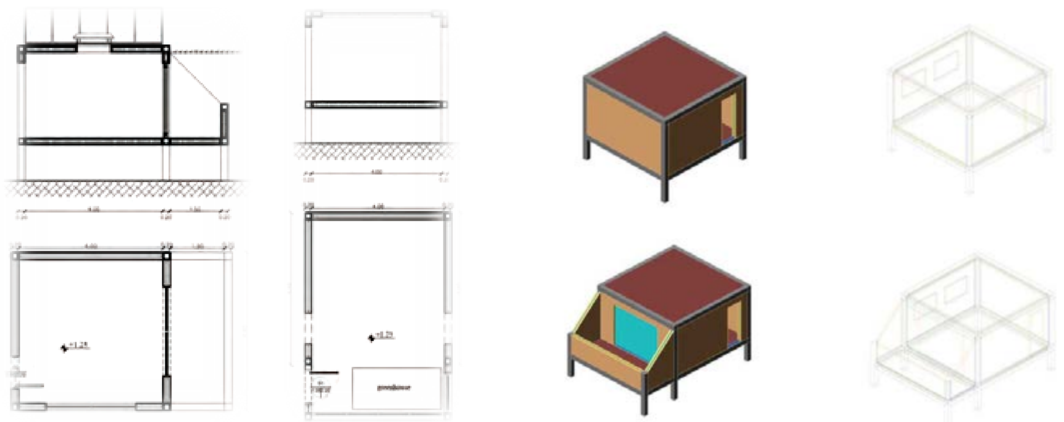


Figure 4. Module 1 (left) and module 2 (center) /3d visualization (right). [5]

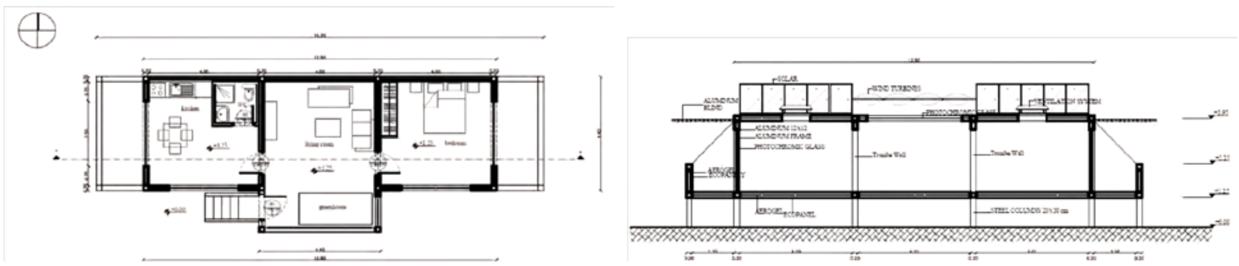


Figure 5. Plan (left) and section of the housing unit. [5]

The project described above claims to be environmentally friendly in all stages of its life cycle, with a minimum of disturbance to the natural environment during construction and low emissions. Environmentally friendly reusable materials are used in the unit. The frame of the unit is made of steel elements, which beyond their primary role as structural elements, serve as guides for the electrical wiring. The walls, floors and ceilings are made from recycled aluminium and insulated

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with mineral wool; they also incorporate a double operation concerning both energy and structure. Those elements are not compact, but they have a honeycomb structure, to ensure low weight structural strength (stiffness) and good energy performance. The prefabricated units can be easily carried in the field or by truck or helicopter because of their low weight.

For the construction and operation of the units in general, advanced materials are largely used, such as photovoltaic thin film, which is effective to diffuse illumination in contrast to conventional ones and photochromic glasses whose optical characteristics vary with the incident solar radiation. Also, aerogel has been used as an insulation material due to its porous and extremely lightweight structure. Furthermore water filters and CO2 filters were used, and also nano-coatings to create hydrophobic surfaces for maximum collection of water, self- cleaning of the outer surfaces and protection of metal components to prevent rust and scratches.

In more detail, the main facade of the unit is facing south in order to utilize the solar radiation. It is made from double glazing and aluminium frame and provides passive solar gains, natural ventilation and lighting. In the south side there is an attached greenhouse to obtain direct solar gains. [6] Shading is achieved by using external louvers. Also, balconies can be converted into semi-enclosed spaces adapting translucent photovoltaic panels, blinds and shades. Both on the west and the east face photochromic glasses are placed. Photochromic glass is also used for the roof openings. Additionally, photovoltaic panels are attached to the roof and photovoltaic thin film on the south, west and east sides, contributing to hot water production. There is also a wind turbine mounted on a metal pole above the roof (horizontal axis wind turbine). Rainwater is collected by means of gutters and filtered through pipes in the tank below the house with special filters. There is also a water reuse system. Second use takes place in the greenhouse and third time on the toilet. Externally facades are planted thus providing extra insulation and the possibility of planting edible plants. In Figure 7 two variations of the prefabricated unit are demonstrated in 3d model.



Figure 7. North, south and top view of the housing unit (left).
General views of the housing unit (right).

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3.3 Environmental assessment

The environmental assessment of the unit and its performance can be tested by using various multicriterion decision methods. In this case, the unit presented in the previous section of the paper was tested on software to determine the overall picture of the operation of the unit, and provided excellent results of heat gains, thermal comfort and energy efficiency. Main software used for the assessment was K-Eco, developed by Dr. Panos Kosmopoulos. It is a user friendly program which fulfils all the requirements that should be met for modern software. Moreover, the results were confirmed by already widely used software such as Retscreen and Ecotect.

The environmental assessment of the shed was based on the climatic data of Xanthi (city in north -east Greece) and Cyprus in order to ensure that the unit can respond as effectively in both climates. The thermophysical characteristics of the materials used are indicated in Table 1. The heating requirements to achieve thermal comfort are much greater in the case of Xanthi, while the opposite happens for the cooling requirements. Big difference in heating requirements are presented during the winter months November -December -January. The calculation of the heating requirements, derived from total heat load from lighting, humans and devices for each month. Based on the results it is shown that the target was achieved as the housing unit works almost as effectively in the two different climatic conditions. In each case the cottage belongs to the category A and A+ respectively, as can be seen in Figure 8. The shed seems to be operating more efficiently in the climatic conditions of Cyprus, but with little difference. It is important to note that it proved effective without taking into account the planted facades as well as the optimization of microclimate achieved with the surrounding planting.

Table 1. Thermophysical characteristics of the materials used on the unit.

Panel material	Thermal conductivity (W/(mK))	Thickness (cm)	Density (Kg/m3)	Specific heat
metal - aluminum	160	1	1800	0,896
Compressed straw	0,102	6	379	0,38
aerogel	0,03	7	3000	0,5
Compressed straw	0,102	6	379	0,38
metal - aluminum	160	1	1800	0,896

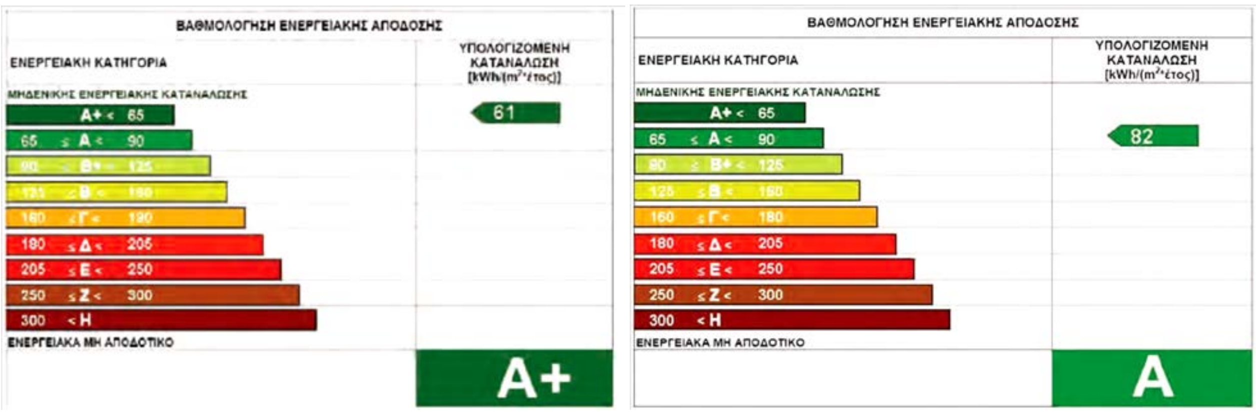


Figure 8. Environmental assessment of the energy identity and behavior of the housing unit based on the climatic data in Cyprus and Xanthi. [5]

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4. CONCLUSIONS

The potentiality of prefabrication of housing units in a large scale will contribute to a rapid and economic solution to meet housing needs resulting from natural and manmade disasters, such as the current refugee crisis. Prefabricated dwellings can be used to cover temporary or more permanent housing needs such as in case of natural disasters. They can even be used to create pilot villages, parks or have other applications e.g. stations -workshops -observatories in remote areas, due to the autonomy and ease of transport and installation. Moreover they can be an environmentally friendly solution, with lower energy consumption and less harmful emissions to the environment, throughout their life cycle.

In any case, and most importantly in an emergency situation, the provided dwelling should not feel uncanny, but should be the means of reintegration into social life. In our view, the quick appropriation of the new residence, will occur if it can meet the personal needs of the habitant and be the first step to restore the rhythms of a pleasant daily routine. The participatory process of creating the dwelling, by completing questionnaires, increases creativity and removes all sense of temporary housing, which gives no room for appropriation.

The issues of sustainable approach of the fabrication and assembly process and the autonomous operation of the unit can be addressed simultaneously, by conducting a life cycle assessment. Bioclimatic behaviour of the housing unit –including the provision of thermal comfort conditions in any climate- can be achieved through the utilization of thermal mass, and the sun to raise the air temperature and ventilation to reduce it. Also, the isolation of rooms is desired for controlling the flow of temperature. Utilization of renewable energy systems (solar panels, wind turbines, photovoltaic thin film) contribute to meet the energy needs of the unit and to achieve self-sufficiency and independence from fossil fuels -if possible, or at least to minimize their use. Managing the water is another key issue, on the autonomous function of the housing unit. Collection and use of rainwater for household activities (watering, cleaning, etc.) can reduce water consumption. In the proposal described, separate pumps are used for drinking water and water for washing and reuse of water. Collecting rainwater should also be included. Facility of composting and recycling is also desired in the plant. In any case, the basic aim is to provide thermal comfort to the inhabitants and be environmentally adaptive in a relatively wide range of climatic conditions.

The target of the presented projects is a bioclimatic human-oriented design, a pre-fabricated housing unit establishing principles concerning respect for the environment and the landscape, the reduction of energy consumption and sustainability in general, and most of all, providing immediate comfort conditions when and where needed. The combination of prefabrication, bioclimatic design, technology and the use of superior materials for green buildings lead to energy efficient construction, long time durability and ease of transportation and adjustment in minimum time. A flexible, sustainable and energy- independent housing unit of rapid development that can respond as effectively in different climatic data both now and in the future is a solution to reduce the energy consumption of the building sector. After all the global climate change phenomenon is something we already experience and is in many cases reason for natural disasters creating homeless people.

References

[1] http://www.unep.org (accessed April 12, 2016).

[2] Alexopoulou E., Roupa, E. 2012. *Mass customization in disaster relief sheltering through activity based design.* Diploma thesis. [ed.] K. Ougrinis and S. Giannoudis. Technical University of Crete, Faculty of Architecture. Chania, Crete, Greece.

[3] Kosmopoulos P., 2008. *Buildings, Energy and the Environment*. University Studio Press, Thessaloniki.

[4] Kosmopoulos P., Voutsas, D. 2010. Proposal on a pre-fabricated eco-settlement. *Econ3.* **12**, 92-07.

[5] Achilleos A., Kosmopoulos, I. 2012. Versatile, sustainable and energy autonomous -rapidly developed- housing unit. *Econ3.* 22, 114-126.

[6] Kosmopoulos P., 2007. *Environmental Design*. University Studio Press, Thessaloniki.

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Bioclimatic design in a modern house with Macedonian architecture elements

K. I. Lantitsou[1*], S. M. Bagiouk[2], G. D. Panagiotakis[1], S. S. Bagiouk[2]

[1] Department of Civil Engineering, Democritus University of Thrace, 67131, Xanthi, Greece.
[2] Department of Civil Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece.
* Corresponding author: Email: klantits@civil.duth.gr

Abstract

Many of the principles of bioclimatic design were the cornerstone of the building during the ancient times and the Byzantine era. Also, these principles are found in many traditional settlements in Greece. It is extremely important that the principles of green building identified in the past structures are able to adapt to modern needs. In the present work there is ab initio design based on the principles of bioclimatic architecture in a modern two-storey building, which has features of traditional Macedonian architecture.

Keywords: traditional architecture; Macedonian architecture; Trombe wall; greenhouse; bioclimatic design.

1. INTRODUCTION

Since ancient times there have been reports on the subject of bioclimatic design in the sense of the ideal home. The one that provides breeze in summer and warmth in winter [1].

Modern needs dictate more spacious houses with large openings in the facades, which are opposed to traditional high thermal mass houses with small openings. Of course, the technology and morphology of the past could not be duplicated today, however, can provide important information in modern design. The principles of green building identified in the past structures are able to adapt to modern needs.

The choice of the location is the starting point of the construction of traditional settlements and housing. The settlements in the continental parts of the Mediterranean develop on the southern slopes of the mountains, so as to the mountain behind them to function as an inhibitor to the northern winds, while the openings of the houses are facing south [2].

Although there are local variations in shape, certain basic features are identified in a Macedonian house. The form of its floor plan in the shape of "Π" creates a central recess, "liakoto", facing directly south. However, the ridge of the house with a roof is rectangular, ensuring the required shading of "liakoto" during summer. Often there is a space attached to the volume of the building or a corridor on the first floor, enclosed by glass windows. In winter the glazing is closed and the area functions as a greenhouse while in summer, it is open and the area functions as a semi-outdoor space that protects the south side of the building from the sun. The heating during the night is achieved by the fireplace in each room, which is usually placed on the north side, so that the generated heat can directly outweigh the cold which is normally present in this side [3].

The capacity of color to act absorbent or reflective depending on its intensity, saturation and brightness appears to be very old knowledge, which was developed very early in buildings. In the northern parts of the mainland one encounters warmer, heat absorbing colours on facades of buildings, such as ocher and terracotta, with a typical example that survives to this day the monasteries of Mount Athos [4].

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In Europe, the building sector is responsible for the 40% of the total energy consumption and the 36% of CO_2 emissions. The European Union created the directive EPBD for the energy efficiency of buildings, aiming at a 20% reduction of greenhouse gas emissions, energy saving and increasing of RES (Renewable Energy Sources) by 2020 [4].

The objective of this study is to initially design a building of modern requirements (as a typical house of a residential complex in the area of Eastern Macedonia), respecting the local traditional architecture, while using bioclimatic design principles. Passive systems were designed and attached to the south side of the building after studying the climatic and environmental conditions in Eastern Macedonia.

2. MATERIALS AND METHODS

2.1 House orientation

The Greek traditional house is constructed having as a rule the southeast orientation, which is considered the ideal orientation (especially for the geographical location of Greece) in order to utilize the sun. In the south it is appropriate to locate the most important functions and those rooms in which the residents spend most of their time (for example the siting of the daily living room is appropriate). Thus, it remains cool in summer, since the rays are high and can be easily prevented with a simple shelter. Furthermore, the arrangement of the additional volumes of the building is such as to create shady corners (protection during summer months). On the contrary, in winter the sun's rays are low on the horizon and thus enter deep into the interior space heating and illuminating the rooms. Finally, with reference to the largest side of the building, it should be oriented to the south with a deviation of 15 degrees (east or west). The specific house is a two-storey traditional building with Macedonian influence with a siting of interiors that utilises each part of the house for the use intended. It has an elongated shape in the east-west axis, thus providing more surface area to the south for the collection of solar heat during the winter months [5].

2.2 Sheltering

The sheltering of the building under study was done with a small sloping roof with a small angle of inclination and ends in a cornice around the building, which protects the exterior walls of the building from rain (Figure 2 and Figure 4). The windows are shaded with the shutters open so that light enters while they can remain open in order to the interior of the building be ventilated. A properly insulated roof enhances the aesthetics of the house and introduces a number of benefits having the tile as the protagonist material. First of all, the tile is impervious to water. Moreover, it is capable of breathing and is non-combustible. Finally, it shows sufficiently high radiation and outside temperature capacity, forming for centuries a traditional way of sheltering [5].

2.3 Layout of spaces

The house meets the general principle of bioclimatic design, which places the South side of the building to use passive solar heating, while the North for protection from the wind and stopping the heat. So, on the north side, which is cooler and requires greater protection from strong winds, the rooms are spaces with a few hours use (e.g. storage, bathroom and guestroom) and secondary spaces that function as a protection zone from cold winds and stop heat loss of the main areas of use. On the other hand, in the southern (and therefore warmer sides of the building) the most residential spaces are placed, that is main use areas (e.g. living room) (Figure 1 and Figure 2). The architecture (e.g. connection of sides, openings) and the siting of the rooms of the residence are not the only elements that make it unique because it simultaneously has passive systems such as a Trombe wall and a greenhouse, designed to give a part of energy independence and saving (Figure 3 and Figure 4).

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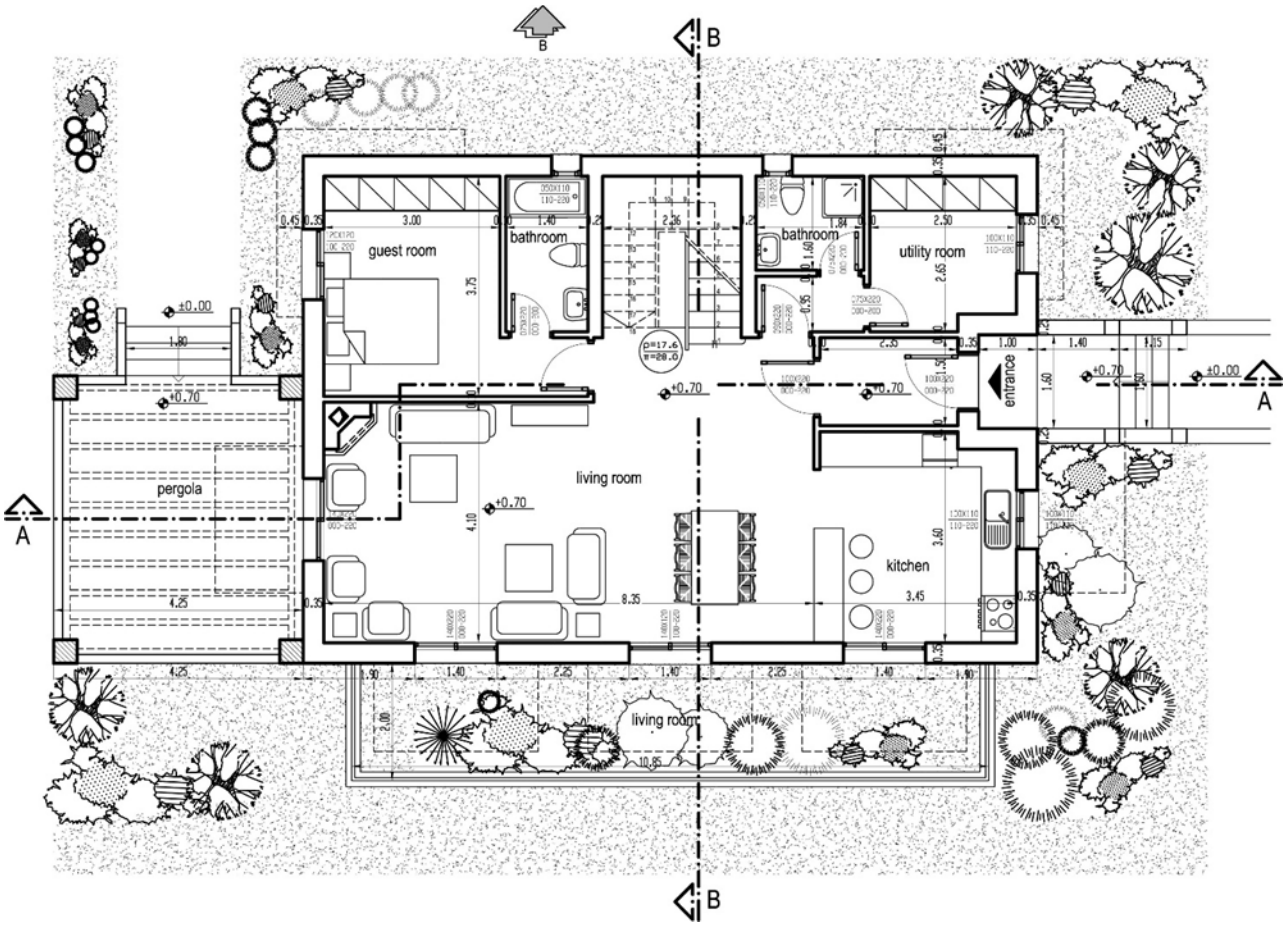


Figure 1. **Ground floor plan view.**

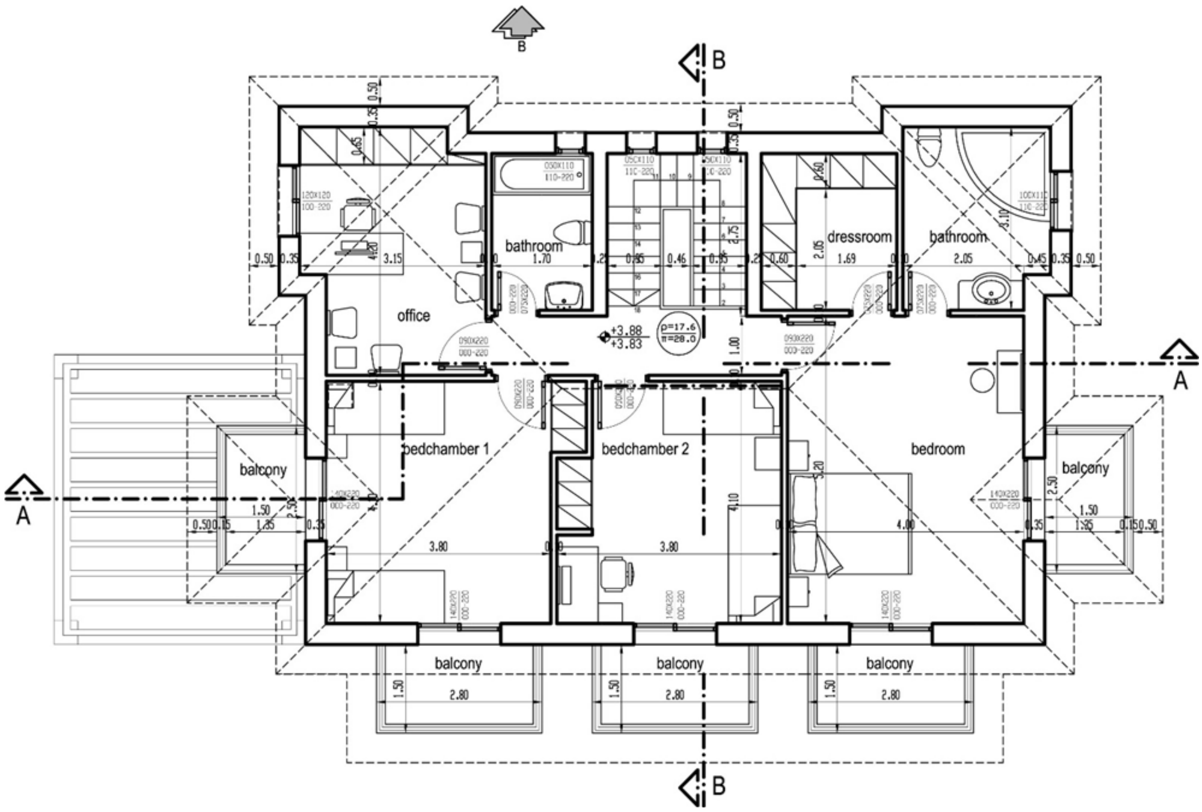


Figure 2. **First floor plan view.**

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2.4 Openings

Large openings to the south, moderate in eastern and western side and smaller to the north are proposed. The largest openings should be oriented to the south while respectively on the north side of the building there should be solid walls and the smallest possible openings. The northern openings of the building should definitely be present, as they provide adequate lighting and through ventilation (mainly in the direction north-south), while they operate as thermal insulation (reduce heat loss). The through-ventilation provides natural cooling in the summer months.

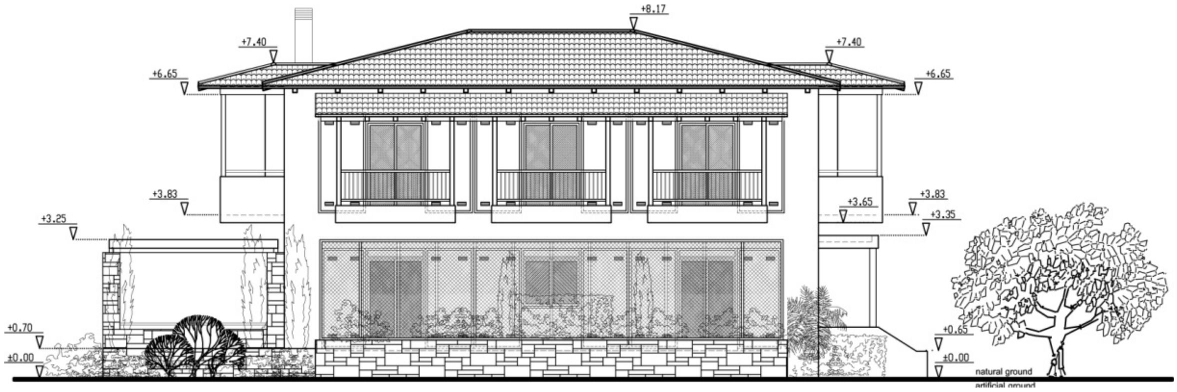


Figure 3. **South view.**



Figure 4. **East view.**

2.6 Dimensioning of southern openings

Considering the relation between the outside temperature and the openings and knowing at the same time the average external temperature of the region (4.5 degrees Celsius), a range was created within the area of the openings will vary, by multiplying the area of each space with its coefficients (Table 1). Using coefficients from semi-empirical formulas [6], the results are:

Living Room, Dining Room, Kitchen Area = 50.48
Minimum Opening Size of Living Room, Dining Room, Kitchen = 50.48m^2 x 0.13 = 6.56 m^2
Maximum Opening Size of Living Room, Dining Room, Kitchen = 50.48m^2 x 0.21 = 10.60 m^2
6.56 < Opening Area <10.60

Minimum Opening Length of Living Room, Dining Room, Kitchen = 6.56 / 2.20 = 2.98
Maximum Opening Length of Living Room, Dining Room, Kitchen = 10.60 / 2.20 = 4.82
2.98 <Opening Length <4.82

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Table 1. Relation between average outdoor temperature in winter and openings

Average outdoor temperature (°C)	Opening Area/floor plan unit
1.7	0.16 - 0.25
4.5	0.13 - 0.21
7.2	0.11 - 1.17

2.7 Pre-dimensioning of Trombe wall

The determination of the Trombe wall area results from its relation with the average outdoor temperature. Using Table 2 [7], in conjunction with the present outdoor temperature of the region (4.5 degrees Celsius), the following results come up:

Living Room, Dining Room, Kitchen Area = 50.48
Minimum Area of Trombe Wall in the Living Room, Dining Room, Kitchen
= $50.48m^2$ x 0.28 = 14.13 m^2
Maximum Area of Trombe Wall in the Living Room, Dining Room, Kitchen
= $50.48m^2$ x 0.46 = 23.22 m^2
14.13 < Trombe Wall Area <23.22

Minimum Length of Trombe Wall in the Living Room, Dining Room, Kitchen
= 14.13 / 3.00 = 4.71
Maximum Length of Trombe Wall in the Living Room, Dining Room, Kitchen
= 23.22 / 3.00 = 7.74
4.71 < Trombe Wall Length <7.74

Table 2. Trombe wall area per $1m^2$ indoor surface according to the average winter temperature

Average outdoor temperature (°C)	Opening Area/floor plan unit
-1	0.43 – 0.78
4.5	0.28 – 0.46

2.8 Pre-dimensioning of the greenhouse

The dimensions of the greenhouse are also subject to the climatic conditions of the region, that is, the average outdoor temperature prevailing in winter (4.5 degrees Celsius). According to Table 3 [7], the following results come up:

Area of the south thermal zone = 50.48
Minimum Area of Glazing = $50.48m^2$ x 0.40 = 20.19 m^2
Maximum Area of Glazing = $50.48m^2$ x 0.70 = 35.40 m^2
20.19 <Glazing Area <35.40

The pre-dimensioning here was not done separately for each room as in the openings and Trombe walls because the space is united with free air flow.

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Table 3. Glazing area (m^2) for $1m^2$ indoor surface combined with thermal storage wall according to the average winter temperature

Average outdoor temperature (°C)	Opening Area/floor plan unit
-1	0.65 – 1.15
4.5	0.40 – 0.70

3. RESULTS AND DISCUSSION

3.1 Passive heating and cooling systems

Passive heating and cooling systems utilize natural energy sources, sun, wind, soil, to heat or cool the building without the interference of mechanical means. Their function is based on the energy exchange with the environment and includes the appropriate storage and distribution of energy within the spaces. Passive systems are components of the building and are included in bioclimatic design.

The system of direct solar benefit is simple in structure and function. It consists of a closed space, serving living or working needs, from the south glazing of which solar radiation is collected and in the spatial mass the heat is stored [5].

To operate properly the system of direct solar benefit there should be a well-structured composition of certain elements. The space should, therefore, has dimensions and proportions to allow sunlight to penetrate in a major part. The glazing should have features that allow the necessary solar annuity during the day in winter, reduce the heat losses during the night, and do not lead to overheating of the area in the summer. [8] Finally, the thermal storage mass should be sufficient to absorb the excess heat during the day and return it in the space at night or when there are clouds.

3.2 Efficiency requirements of passive systems

The proper orientation of the buildings is a prerequisite for the use of solar energy and for their heating. The southern orientation offers the best potential for the exploitation of solar energy by ensuring more effective insolation hours in winter and at the same time the possibility of shading in summer.

The biggest problem for effective implementation of passive systems occurs in large urban centers, and more generally in dense areas, in relation to the siting of buildings on the land, the orientation and the shading from the opposite buildings. For this reason, it is understood that there is no such thing as bioclimatic design of a building but bioclimatic design of a settlement.

By thermal analysis carried out in buildings with passive solar systems attached to the side using software (Ecotect Analysis 2011), with proper indoor arrangement and seamless southern insolation, it is known that saving for cooling can be up to 28% [9] and for heating up to 27.5% [10]. The reduction of thermal needs for heating and cooling is even more impressive, if only the living rooms and bedrooms on the south side are considered, where the total saving is up to 45% [9].

Even with the attachment of the greenhouse and Trombe walls that were applied in this study, it is not possible to have energy independence throughout the year with the present architectural concepts in terms of volumes and the size of the openings. For this reason, the use of RES is proposed to cover the additional energy requirements.

One suggestion is the shades are of PV modules [11] or even a part of the roof could be covered with solar panels, offering electricity from the sun and heat insulation to the building [12].

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4. CONCLUSIONS

In conclusion there could be a combination of traditional architecture and specifically the traditional Macedonian in a contemporary bioclimatic building. It could be said that the solutions to the problem of energy saving in the building sector derive from the past. The addition of passive systems such as Trombe wall and greenhouse, with appropriate design based on the climatic characteristics of the region, can save energy for heating up to 46.6% as well as cooling up to 39.5% for the southern thermal zones, while maintaining the traditional architecture elements.

References

[1] Papageorgioy A., 1993. *Xenofon the Athenian, Complete Works 1 – Memoir 1*. Kaktos, Athens.

[2] Tzelepis P., 1997. *Greek Folk Architecture.*Themelio, Athens.

[3] http://www.ntua.gr/MIRC/db/epirus_db/ARXITEKTONIKH/Perivallontikes%20parametroi.htm (accessed December 15th, 2015).

[4] http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=URISERV%3Aen0021 (accessed December 10th, 2015).

[5] Tsipiras K., 1996. *The Eco-house*. Nea Sinora – A. A. Livani, Athens.

[6] Axarli K., Giannas S., Evangelinos E., Zaharopoulos E. & Marda N., 2001. *Bioclimatic design of buildings and surroundings.* Volume A, Greek Open University, Patra.

[7] Perdios S., 2007. *Energy-saving Interventions in buildings - sports centers - industries - transport.* Volume A, Selka 4M, Athens

[8] European Commission, 1998. *Energy in Architecture, The European Manual for Passive Solar Buildings.* Malliaris Education, Athens.

[9] Lantitsou K. and Panagiotakis G., 2012. Bioclimatic Design of a Settlement – Based on ECOTECT software. *1st Environmental Conference of Thessaly* (eds. A. G. Kungolos, O. Christopoulou, C. Laspidou), September 8–10, Skiathos Island, Greece, 375–382.

[10] Lantitsou K. and Panagiotakis G., 2015. Dwelling Passive Solar Retrofit. *2nd Environmental Conference of Thessaly* (eds. K. Perakis, A. Kungolos, C. Laspidou, O. Christopoulou), September 26–28, Skiathos Island, Greece, 203–209.

[11] Mandalaki M., Papantoniou S. and Tsoutsos T., 2014. Assessment of energy production from photovoltaic modules integrated in typical shading devices. *Sustainable Cities and Society*, **10**, 222–231.

[12] Bahaj A.S., 2003. Photovoltaic roofing: Issues of design and integration into buildings. *Renewable Energy*, **28(14)**, 2195–2204.

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Research on how buildings and covering materials affect microclimate conditions: Case study the center of Thessaloniki

A. Kantzioura, P. Kosmopoulos*

Laboratory of Environmental and Energy Efficient Design of Buildings and Settlements,
Democritus University of Thrace, 67100, Xanthi, Greece.
*Corresponding author: Email: pkosmos@env.duth.gr

Abstract

The urban planning, the buildings and the covering materials of all surfaces, the distance between adjacent buildings, the height and the orientation of the buildings are some of the factors which affect the comfort conditions in the city.

This paper presents a project that aims at investigating the influence of urban developments in microclimatic conditions. The purpose of the research is to investigate how the characteristics of the built environment contribute the microclimatic conditions.

A number of experimental procedures were carried out. The gathered data came from two different study areas in the urban center of Thessaloniki, so as the geometric characteristics (eg H/W ratio), the morphology and the construction materials to be different. The research analyses how the microclimate parameters are affected by the urban geometry and construction materials.
The study focuses at the variation of air temperature, surface temperature, wind speed and wind direction on a 24 h basis within urban canyons. Also, the research studies the correlation between microclimatic parameters and the geometric characteristics of urban morphology.

The results of the analysis conclude that the surface temperatures and microclimatic conditions are differentiated along the streets, on different heights and orientations, and also according to urban planning. The results of the investigation could contribute at the optimum design solutions in response to climatic changes, and toward the sustainable development of the contemporary cities.

Keywords: microclimate; urban centers; surface temperature.

1. INTRODUCTION

The covered and construction materials in contemporary cities and the urban geometrical characteristics affect the microclimatic conditions inside the urban centers [1]. The radiant balance of the urban space, the convective heat exchange between the ground and the buildings, the air flowing above the urban area and the heat generation within the city [2][3] increase the air temperature in the city. The city had the capacity to modify local climate, and even created environmental conditions that could be regarded an urban microclimate [4][5]. According to Wong et al., there are three elements that affect urban temperature on a local scale: buildings, green spaces, and pavement [6].

In previous studies the microclimatic conditions in urban canyons are analyzed [7][8]. The present paper study the thermal behaviour of vertical surfaces in urban canyons, the air temperature, the correlation between them and the effect of H/W in microclimatic conditions.

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2. METHODOLOGY

A number of experimental procedures were carried out in order to investigate the effect of urban planning on microclimatic conditions. The first study area is located in the urban center of Thessaloniki, Greece in the crossway Metropoleos and Agias Sofias Street, and it consists of high building blocks. The second study area is located in Triandria, Thessaloniki, Greece (Figure 1) and it consists of high building blocks for residential use. It is adjacent to the urban center of the city.

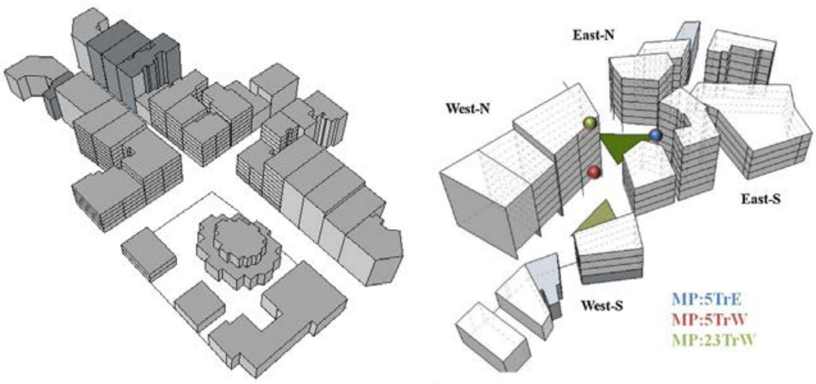


Figure 1: Study area in Urban Center of Thessaloniki, Greece (created with SketchUp)

Data from different measurement points along the streets, from different heights and orientation were collected. The data gathered investigate the variation of Surface Temperature (T_{surf}) on a 24 hours' basis and Air Temperature (T_{air}). The measurements took place during all seasons of the year. The field surveys involve surface temperature measurements by a thermal camera and microclimatic monitoring with portable mini-weather stations. The mini weather stations for monitoring the microclimatic conditions were placed in specific fixed Measurements Points (MP) in the study area, in different heights along the street. In present paper the research is focused in Air Temperature. Also, data from one local meteorological station in the urban centre (near to study area) and form the suburban area of Airport were used to compare the microclimatic parameters of the Greater Thessaloniki Area (GTA), of the urban centre and of the study areas. Specifically, the vertical surface temperatures are measured for each floor, of each building in the study area. So, in each side of the road the surface temperatures of continue buildings' facades are observed.
Also, mini portable weather stations were placed in representative MPs, in order to investigate parameters of urban microclimate and specifically Air Temperature.

The geometric characteristics of the streets are given in Table 1. The average Height is referred to the average height of the buildings in the street, the Length of the street describes the distance of the urban canyon and the ratio H/W is a geometric characteristic to describe the urban canyon. The urban canyon in urban centre orientated in the West and North Street, and in residential area (Triandria) in the axis West-East.

Table 1: Geometric Characteristics of urban canyons

Study area	Orientation	Av. Height H (m)	Str Length, L (m)	Av Str Width, W (m)	H/W
	West	23	60	12.5	1.8
	North	21	70	14	1.4
Urban center	East	21	100	14	1.5
	South	18	50	14	1.3
Residential	West	20	50	7	2.9
Area	East	19	35	7	2.7

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3. RESULTS AND DISCUSSION

3.1 Vertical T_{surf} in urban center

Table 2 is referred to the maximum surface temperatures in the urban center. It summarizes the time of maximum surface temperature in the center, the value of the maximum surface temperature and the floor that max T_{surf} is observed. For each examined Building it gives the greater temperature that was measured by the thermal camera.

Table 2: Maximum surface temperatures

		Building 1			Building 2			Building 3		
		Time	$T_{surface}$ (^{O}C)	Floor	Time	$T_{surface}$ (^{O}C)	Floor	Time	$T_{surface}$ (^{O}C)	Floor
West-S	May	14:00	27.3	1st	16:00	26.3	1st	14:00	26.4	1st
	July	16:00	32	2nd	16:00	33.3	4th	14:00	32.1	4th
	August	15:00	33.1	3rd	15:00	32.6	5th	14:00	33.4	1st
West-N	May	16:00	27.5	5th	14:00	30.1	2nd	14:00	32.1	6th
	July	16:00	35.3	5th	17:00	38.6	5th	15:00	38.1	6th
	August	16:00	38.3	5th	15:00	42.6	4th	15:00	39.6	6th
North-E	May									
	July	18:00	34.7	2nd	17:00	34.9	2nd	18:00	33.4	3rd,8th
	August	18:00	35.8	2nd	17:00	35.7	2nd	17:00	34.6	1st
North-W	May	11:00			11:00			12:00		
	July	10:00	36.6	5th	10:00	40.1	3th	12:00	34.8	3rd
	August	11:00	37.6	5th	11:00	40.3	2nd	11:00	35.8	5th
East-S	May									
	July	16:00	31.7	2nd						
	August	18:00	33.3	1st						
East-N	May	16:00	28.9	1st	18:00	30.9	1st	18:00	28.3	1nd
	July	17:00	37.8	1st	17:00	37.8	2nd	17:00	35.7	3rd
	August	16:00	40	1st	17:00	38.7	2nd	17:00	37.6	1st
South-E	May									
	July	18:00	37.2	1st	17:00	32	Ground floor			
	August	17:00	35.3	Ground floor	17:00	32.2	Ground floor	17:00	32.4	Ground floor
South-W	May	12:00	31.4	2nd		29.5	2nd	11:00	28.1	2nd
	July	10:00	40.6	1st	10:00	37.2	3rd	10:00	38.2	1st
	August	12:00	40	2nd	11:00	39	2nd	11:00	37.9	1st

The analysis of T_{surf} variation indicates different thermal behavior of the vertical surfaces according to the measurement height (floor of the building), the orientation, the location within the urban canyon, the distance of the MP from the crossway and the time of the day.

In the West orientated urban canyon, the maximum temperature of vertical surfaces is observed at 14:00-16:00pm, for both of the two sides of the road (West-S and West-N). In West-N side greater T_{surf} appears on the first floors of the buildings, while in the West-S side on higher floors. Also, the Measurement Points closest to the crossway have greater T_{surf} than inside the urban canyon.

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In North orientated urban canyon, in North-E side the maximum surface temperature occurs at afternoon at 17:00-18:00p.m., while in North-W at the morning, 10:00-11:00a.m. The side's orientation and the sun's position influence the thermal behavior of vertical surfaces and the time that maximum surface appears. In the North-E side, higher surface temperatures observed on first floors of the buildings, while in the North-W side on the middle and upper floors. The T_{surf} is greater in the west side of the road due to the duration of solar radiation (Fig.2). Also, the Measurement Points closest to the crossway have greater T_{surf} than inside the urban canyon in the majority of the measurement data.

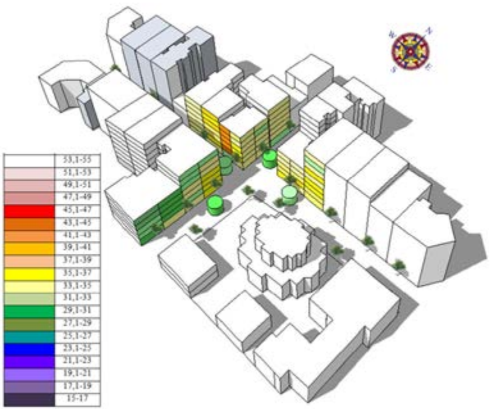


Figure 2: Temperature variation of vertical surfaces (created with SketchUp)

In the East orientated street, a lower height building (church) is located on East-S side of the road. The max T_{surf} is observed at 16:00-18:00 pm (Figure 3). The maximum temperatures of vertical surfaces are observed at lower heights and in locations at a distance from the crossway. The south or north side of the road don't affect the thermal behavior of the vertical surfaces, as they appear the same daily temperature variation.

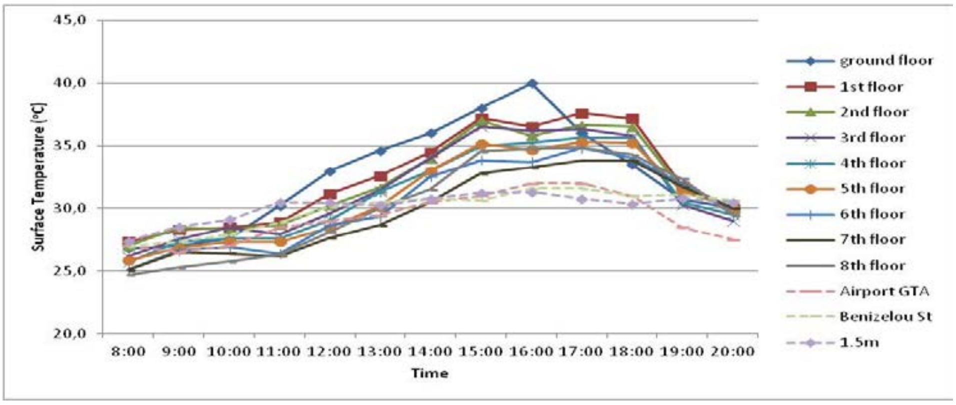


Figure 3: Surface temperature of vertical building façade, Building 2, East-N side, August

In South-E orientated side, the maximum surface temperature occurs at the afternoon, 17:00 pm, while in the South-W side during morning time, 10:00-12:00am. The max T_{surf} observed on the first floor and in the building near to the crossway.

Concluded, the road located on the North-South axis appears different thermal behavior according to the orientation of each side of the road. The vertical surfaces of buildings' façade on west side develop high temperature during morning time, while on east side at the afternoon. Greater T_{surf} is observed at west side. On West-East axis road, the maximum surface temperature is observed mainly during evening hours. The orientation of each side of the road doesn't affect the

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thermal behavior of the surfaces, as observed in the North-South axis.

3.2 Correlation between vertical T_{surf} and T_{air} on pedestrian's level, in urban center

The correlation coefficient ρ is used below in order to investigate the correlation between the T_{surf} and T_{ai}r. The T_{air} on pedestrian's level on 1.5m height was measured by mini portable station during 24hrs basis. In Table 3 the correlation between the T_{air} on pedestrians' level (1.5m) and T_{surf} for each floor is estimated.

The correlation between the T_{air} on 1.5m height and T_{surf} is greater to closest vertical surfaces (ground floor and 1st floor). As the distance from the pedestrians' level is higher so the ρ is decreasing. The correlation between air temperature on 1.5m height and surface temperature of ground floor facade is about 0.8 to 0.9. In July, the correlation is less than in May and August.

Also, in North and West orientated urban canyons, the correlation coefficient is higher than in the East and South orientated street, where there is a low building on one side of the road.

Therefore, the urban morphology affects the microclimatic conditions within an urban canyon. In the streets where there are no high buildings on either side of the roads, there is no correlation. In the urban canyons (West and North street), it is observed that when the surface temperature of the ground floor is increasing then the air temperature is warming on the pedestrian's level.

Table 3: Correlation between T_{air} on 1.5m height and T_{surf}

		ρ (Tsurf-Tair,1.5m)						
		ground floor	**1st floor**	**2nd floor**	**3rd floor**	**4th floor**	**5th floor**	**6th floor**
West-S	May	0.86	0.73	0.58	0.69	0.64	0.63	0.64
	July	0.76	0.67	0.30	0.31	0.02	0.21	0.30
	August	0.89	0.89	0.82	0.85	0.86	0.80	0.84
West-N	May	0.90	0.75	0.67	0.74	0.74	0.68	
	July	0.68	0.72	0.71	0.72	0.77	0.79	
	August	0.85	0.77	0.79	0.85	0.83	0.82	
North-E	May							
	July	0.72	0.67	0.64	0.67	0.56		
	August	0.90	0.73	0.71	0.80	0.83		
North-W	May							
	July	0.72	0.39	0.29	0.27	0.31	-0.18	
	August	0.75	0.61	0.37	0.28	0.70	0.28	
East-S	May							
	July	0.62	0.68					
	August	0.78	0.71					
East-N	May	0.76	0.57	0.71	0.76	0.64		
	July	0.62	0.72	0.72	0.71	0.74		
	August	0.83	0.79	0.80	0.80	0.84		
South-E	May							
	July	0.69	0.76					
	August	0.77	0.74					
South-W	May		0.46	0.56	0.26	0.41	0.37	0.47
	July	0.08	-0.28	-0.63	-0.58	-0.46	-0.46	-0.34
	August	0.70	0.44	0.26	0.33	0.28	0.34	0.36

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The urban morphology influences the urban microclimate and the outdoor thermal comfort conditions. The temperatures of the vertical surfaces and the urban geometric characteristics are factors that affect the air temperature at low altitude.

3.3 Vertical T_{surf} in urban center in Residential area

During summer period, in West-N the maximum T_{surf} is observed at 18:00, while at October it is observed at 16:00-17:00 (Figure 4). Greater surface temperatures are developed inside the urban canyons. In August the maximum T_{surf} and maximum T_{air} are observed at the same time (18:00), while in October, the maximum T_{air} is appeared 2-3 hrs earlier at 14:00 than the maximum T_{surf}.

In West-S, the maximum T_{surf} are observed during the morning time, in contrast to the West-N side where the maximum T_{surf} are observed at afternoon. The air temperature on the pedestrian's level rises until afternoon at 18:00.

Comparing the T_{surf} of measurement points on different heights, shows that the maximum values are observed at low level heights, at both sides of the west orientated road (Table 4).

In the East road the maximum T_{surf} are observed in MPs near to the crossway.

In side East-S, the maximum surface temperature occurs at different times in different locations along the urban canyon (Table 5). In July the maximum T_{surf} is observed at 15:00-17:00, in August earlier at 11:00-15:00, and in October at 11:00. During the summer period (August), in the first building the maximum value is observed at 15:00. Regarding the next buildings inside to the urban canyon on East-EW Street, the maximum surface temperature is observed later. Specifically, the Building2 reaches the maximum one hour later, the Building3 two hours later and the Building3 four hours later. In October the maximum T_{surf} is observed at 11:00 in all buildings along the urban canyon.

Comparing the surface temperatures shows that during the summer the maximum values are observed near to the crossway, while on October inside the urban canyon

The maximum T_{air} on pedestrian's level is observed some hours later than the max T_{surf}..

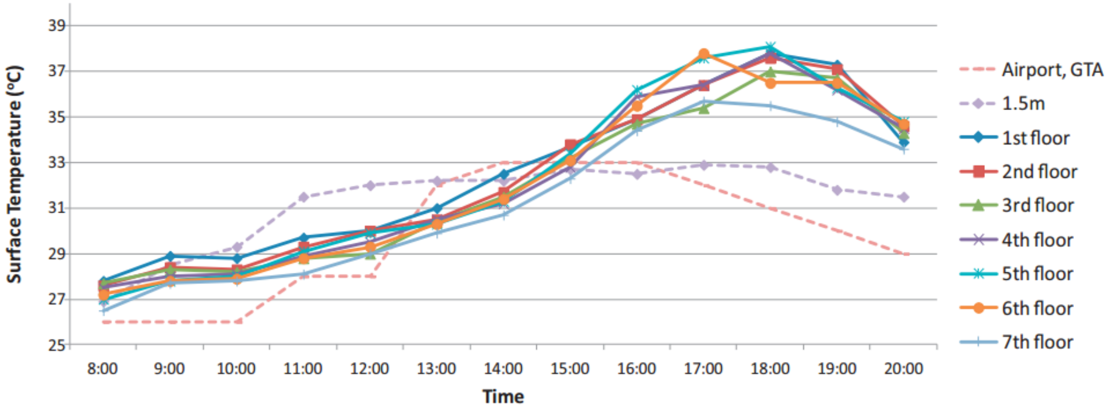


Figure 4: Surface temperature, building 1/1, West-N, July

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Table 4: Time of maximum T_{surf}, West

		Building 1/1			Building 2			Building 3		
		Time	$T_{surface}$	Floor	Time	$T_{surface}$	Floor	Time	$T_{surface}$	Floor
West-N	JUL	18:00	38.1	5th						
	AUG	18:00	48.5	1st	18:00	48.1	3rd	18:00	46.8	1st
	OKT	17:00	37.3	1st	17:00	41.4	1st	16:00	40.9	2nd
West-S	JUL	11:00	38.5	2nd						
	AUG	13:00	44.1	1nd						
	OKT	11:00	46.6	Ground fl						

Table 5: Time of maximum T_{surf}, East

		Building 1			Building 2			Building 3			Building 4		
East-N	JUL	17:00	35.5	1st	17:00	37.9	1st						
	AUG	16:00	38.1	1st	19:00	36.6	1st						
	OKT	17:00	42.6	1st	17:00	35.3	1st						
East-S	JUL	8:00	35.7	1st	15:00	32.8	1st	17:00	34.6	3rd			
	AUG	15:00	36.4	2nd	14:00	39	1st	13:00	42.3	2nd	11:00	39.3	2nd
	OKT	11:00	42.3	2nd	11:00	50	1st	11:00	53.6	1st	11:00	53.8	2nd

3.4 Correlation of T_{surf} and T_{air} in Residential area

The correlation coefficient ρ is used below in order to investigate the correlation between the T_{surf} and T_{air}. In Table 6 the correlation between the T_{air} on pedestrians' level (1.5m) and T_{surf} for each floor is estimated.

The correlation is greater at northern sides of both the west and east street. The correlation coefficient in north sides is about 0.7-0.95. In southern sides the correlation is insignificant, mainly in October.

Table 6: Correlation of T_{surf} on different floors and T_{air} on pedestrians' level

		$\rho_{\text{(Tsurf-Tair,1.5m)}}$							
		ground	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**
West-N	July		0.73	0.72	0.69	0.71	0.74	0.72	0.74
	August		0.90	0.90	0.91	0.93	0.93	0.92	0.93
	October		0.85	0.88	0.80	0.84	0.82	0.81	0.85
West-S	July	0.89	0.71	0.42	0.26				
	August	0.86	0.83	0.83	0.79				
	October	-0.03	0.04	-0.02	-0.01				
East-N	July		0.95	0.93	0.89	0.88	0.86	0.84	
	August		0.95	0.90	0.90	0.91	0.92	0.92	
	October		0.70	0.68	0.68	0.72	0.67	0.61	
East-S	July		-0.12	-0.43	-0.65	-0.55			
	August		0.75	0.82	0.75	0.72			
	October		0.10	0.02	0.04	0.05			

In Table 7 the correlation between the T_{air} on 5m height ($(T_{air})_{5TrE}$ and $(T_{air})_{5TrW}$) and T_{surf} of the first floor (T_{surf})1st is calculated, as well the correlation between the T_{air} on 23m height ($(T_{air})_{23TrW}$) and T_{surf} of the 7th floor.

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Table 7: Correlation of T_{surf} and T_{air} in different measurement heights.

			July	August	October
Residential area	East-S	$(T_{surf})_{1st}$-$(T_{air})_{5TrE}$ $(Tair)_{5TrE}$	-0.167	0.685	0.152
	Wesr-N	$(T_{surf}f)_{1st}$--$(T_{air})_{5Trw}$ $(Tair)_{5TrW}$	0.969	0.778	0.714
	Wesr-S	$(T_{surf})_{7st}$--$(T_{air})_{3Trw}$ $(Tair)23_{TrE}$ $(Tair)_{23TrW}$	0.957	0.796	0.870

Comparing the coefficient ρ between the T_{surf} and the T_{air} for the same measurement height, shows that in the West-N side the correlation is satisfactory (ρ=0.8-0.9). The ratio H_1/H_2 in west orientated street (H_1/H_2=1) is lower than East. In East Street the ρ is almost zero.

4. CONCLUSIONS

In Table 8 the Air Temperature differences between 20:00pm and 8:00am. at pedestrian's level, for the urban center and residential area are shown.

The T_{air} in urban center at afternoon is about 3^{o}C higher than in the 8:00 am. In the East orientated street, the T_{air} is 7^{0}C higher in May, which affects negatively the thermal comfort conditions at pedestrian's level.

The differences in residential area, the ratio H/W is greater that center, are higher. The maximum difference is observed during October and it reaches the 10^{o}C.

So the geometric characteristics affect the microclimatic conditions, specifically the T_{air}. The building's height and the roads width prevent the cooling of urban canyon and the T_{air} remains high for long time after the sunset.

Table 8: Air Temperature differences between 20:00pm and 8:00am. at pedestrian's level

	Urban center				GTA	Residential area		GTA
	West	**North**	**East**	**South**		**West**	**East**	
May	3.3 ^{o}C		7.0 ^{o}C	3.3 ^{o}C	2.5 ^{o}C			
July	3.3 ^{o}C	2.7 ^{o}C	2.8 ^{o}C	3.1 ^{o}C	3.0 ^{o}C	4.6 ^{o}C	3.4 ^{o}C	3 ^{o}C
August	2.9 ^{o}C	3.6 ^{o}C	3.1 ^{o}C	3.8 ^{o}C	0.5 ^{o}C	6.2 ^{o}C	6.2 ^{o}C	6 ^{o}C
October						8.1 ^{o}C	10.0 ^{o}C	8 ^{o}C

Finally, in conclusion the urban morphology influences the surface temperatures, the microclimatic parameters in the urban centers and affects the conditions inside the urban canyons.

References

[1] Lau, S. S. Y., Yang, F., Tai, J., Wu, X. L., & Wang, J., (2011), The study of summer-time heat island, built form and fabric in a densely built urban environment in compact Chinese cities: Hong Kong, Guangzhou. International Journal of Sustainable Development, Vol. 14(1-2), pp. 30-48

[2] Mihalakakou, P., Flocas, H.A., Santamouris, M., Helmis, C.G., (2002), Application of neural networks to the simulation of the heat island over Athens, Greece, using synoptic types as a predictor. Journal of Applied Meteorology, Vol. 41 5, pp. 519–527.

[3] Santamouris, M., Mihalakakou, G., Papanikolaou, N., Assimakopoulos, D.N., (1999), A neural network approach for modeling the heat island phenomenon in urban areas during the summer period. Geophysical Research Letters, Vol. 26 3, pp. 337–340.

[4] Gago E.J., Roldan J., Pacheco- Torres R., Ordóñez J., The city and urban heat islands: A review of strategies to mitigate adverse effects, Renewable and Sustainable Energy Reviews, Volume 25, (2013), pp.749–758

[5] Giridharan R, GanesanS, LauSSY. Day time urban heat island effect in high- rise and high-density residential developments in Hong Kong. Energy and Building, Volume 36, (2004), pp. 525–34.

ISBN: 978-960-6865-94-7

[6] Wong NH, Jusuf SK, Syafii NI, Chen Y, Hajadi N, Sathyanarayanan H, Manickavasagam Y. Evaluation of the impact of the surrounding urban morphology on building energy consumption. Solar Energy, Volume 85, (2011) pp. 57–71.
[7] A. Kantzioura, P. Kosmopoulos, A. Dimoudi, S. Zoras, 2015, Experimental investigation of microclimatic conditions in relation to the built environment in a central urban area in Thessaloniki (Northern Greece): A case study, Sustainable Cities and Society, Available online 20 March 2015, ISSN 2210-6707, http://dx.doi.org/10.1016/j.scs.2015.03.006.
[8] Panos Kosmopoulos, Athina Kantzioura, 2014, Effects of urban development in microclimatic conditions in Thessaloniki, Global Nest, Volume 16, Issue 5, pp 840-855.

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Air quality
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PROTECTION
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OF THE
ENVIRONMENT
XIII

Behavior and impact on the environment of fire retardants in cars

A. Athanasopoulou*, V. Kollarou, G. Kollaros

Department of Civil Engineering, Democritus University of Thrace, 67132, Xanthi, Greece.
*Corresponding author: Email: anatha@civil.duth.gr

Abstract

In an effort to assist the understanding fire retardant substances, their behaviour is addressed. Polybrominated diphenyl ethers have been used in the transportation industry. Emphasis is given to their chemical characteristics and behaviour under special temperature conditions, age of the vehicle, indoor ventilation, and other factors. Bio-concentration and bioaccumulation in the environment is due to their high binding affinity to particles and lipophilic characteristics. Congeners of polybrominated diphenyl ether continue to be detected in the environment and in humans, though commercial products containing these toxic substances have been phased out. The most comprehensive measurements and analyses found in the literature are briefly described and comparisons for the different available data and results are discussed. All reviewed studies demonstrate car interiors being contaminated with brominated fire retardants.

Keywords: brominated fire retardants; polybrominated diphenyl ether; automobile; debromination

1. INTRODUCTION

Automobiles are hosting drivers and passengers a considerable time fraction of the day (5-6%) while travelling from home to work or during other activities, like shopping and recreation [1]. The World Health Organization (WHO) has recognized the interior air pollution of vehicles as a major threat to human health [2]. House dust provides a major contribution to human exposure due to the time spent there, much higher than in cars.

By the end of 2013, a mixture used as a fire resistant additive to every day products, named DecaBDE has been phased out. The main reason for that decision is the impact it has to the environment, living organisms and humans -especially toddlers. People spending a considerable amount of time in cars or other types of vehicles (taxi drivers, truckers, commercial representatives promoting products in distant places, etc) are particularly affected through inhalation or digestion of semi-volatile organic compounds commonly added to consumer products found in various microenvironments including accessories in means of transportation.

A wide variety of polymers with different properties have been introduced in clothing, furniture, electronics, computers and vehicles over the past 50 years. Since the majority of polymers contained in cars are petroleum based (several kilograms of cables) are flammable, the safety regulations require the use of materials added or applied to increase the vehicle's fire resistance [3]. A range of materials that fulfil this requirement are found in the market under the general name brominated flame retardants. These substances can inhibit fire ignition or slow the combustion rate. Depending on the mode they are incorporated to polymers can be divided in brominated monomers, reactive, and additive (including hexabromo-cyclododecane, HBCD, and polybrominated diphenyl ethers, PBDEs) [4]. Tetrabromobisphenol A (TBBPA) is chemically bonded into plastics, hence an example of reactive brominated flame retardant. PBDEs, HBCD and TBBPA are commonly used BFRs in vehicles (in the ABS, instrument panel, nylon connectors, wire insulation, floor coverings, vehicle electronics, upholstery like fabric backing and arm rests, etc).

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In the 1960s, the production of PBDEs started. They are semi-volatile organic compounds added to consumer products at percent levels and they theoretically involve 209 congeners numbered using the IUPAC (International Union of Pure and Applied Chemistry) system, but in commercial mixtures are fewer [5]. The most used formulations are Penta-, Octa-, and DecaBDE. They have high affinity to particles with lipophilic characteristics. Due to this tendency, they may be found in the environment even after several years, bearing in mind that sources of the formulations could be found even nowadays [6].

High percentage (40%) of vehicle interiors in a 2011-2012 vehicle screening contained brominated fire retardants (BFRs) [7]. Technical grades of PentaBDE have historically been used in automobiles in polyurethane foams. Applications of DecaBDE in automobiles and mass transportation means include fabric, reinforced plastics, under the hood or dash, and electric & electronic equipment (battery case and tray, engine control, electrical connectors, components of radio disk, GPS and computer systems).

In automobiles, dust particles bearing polybrominated diphenyl ethers could be formed by volatilized PBDEs from interior foam and electronic components or could have their origin in the aging or the abrasion of polymers containing PBDE. Automobile dust vacuumed from British car seats when undergone scanning electron microscopy with energy dispersive spectrometry has been shown to be highly inhomogeneous in bromine distribution and BDE 209 originates from the abrasion of fabric treated with DecaBDE [8].

If an adult inhales 20 m^3 air/day then a driver inside a contaminated car would receive 54 ng of PBDEs through inhalation in 8 hours. Estimates on the inhalation intake in various environments suggest that the exposure to PBDEs during an 80-min drive is approximately equivalent to the exposure from 16.5 hours at home or eight hours at work [9].

2. POLYBROMINATED DIPHENYL ETHERS IN PRIVATE CAR AIR AND DUST

Airborne concentrations of principal PBDE congeners monitored in various studies [10, 11] were measured in 31 homes, 33 offices, a coffee shop, a supermarket, a post office, and 25 cars in UK [12]. Deca-bromodiphenyl ether was not included because it was difficult to reliably determine it. Indoor air samples were collected using polyurethane foam (PUF) disk passive samplers. Public transport was considered unsuitable for sitting passive air samplers. Probably, the PUF disk air samplers underestimate concentrations of the higher molecular weight congeners, as these are more associated with the particulate phase. More than 50% of BDEs 153 and 154 have been observed to be present in the particulate phase in indoor air [10]. Therefore, the aforementioned effect will be more marked for these congeners. Cars are the most contaminated microenvironment where average ΣBDE equals to 709 pg/m^3 with major contributors to ΣBDE being the congeners 47 and 99 [12].

Ten houses, 44 apartments, 10 day care centres, 10 offices and 17 cars were the places in the Stockholm City area where from samples were analyzed for tri- to deca- BDEs found in three technical Penta-, Octa- and DecaBDE products [13]. In all air and dust samples PBDEs were detected. All cars were new. The samples had been taken indoors with the fan on to simulate ventilation during locomotion conditions. Seventeen cars manufactured by seven different industries were sampled having their windows closed. Five cars from two different manufacturers were sampled twice, once while indoors at room temperature, and a day later standing in the sunshine with the windows closed to reach a higher indoor temperature. In addition, indoor air samples were taken in two of the dealership garages. In car air the median ΣPBDE concentrations were 520 pg/m^3. Further analyses performed on the samples from the Stockholm City area by Thuresson et al. [14] showed that in cars, median ΣPBDE concentrations in air was 510 pg/m^3 and in dust 1,400 ng/g (only 4 cars sampled). For all microenvironments, the brominated flame retardant found in highest concentration in air was ΣDecaBDE, primarily BDE 209, followed by ΣPentaBDE,

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and in dust, ΣDecaBDE, followed by HBCD. Positive correlations were found between matched air and dust samples for ΣPentaBDE, but not for ΣDecaBDE. The concentrations and BDE congener profiles in air samples from the dealership halls and the cars sampled in the same halls were similar.

In Greece, Sweden and UK, different median concentrations of PBDEs in car air have been recorded [15]. The works of Mandalakis et al. [16], Thuresson et al. [14] and Harrad et al. [12] have reported median total concentrations of 201 pg m^{-3}, 510 pg m^{-3}, and 41 pg m^{-3} ΣPBDE respectively for 18 including BDE-209 10 including BDE-209 and 9 not including BDE-209 congeners. BDE-209 was the most abundant congener accounting for 38-66% of total PBDEs

In a nine month period dust samples were collected from 9 living rooms and 8 offices within the West Midlands conurbation as well as from 8 cars [17]. The surface of the car seats (not including seat backs), the front panel, and the steering wheel were sampled for 2 minutes. Targets of the analysis were BDE 47, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 208, and 209. Debromination of BDE 209 was indicated by factors like the profile and ratios of nona BDEs, the detection of BDE 202, and the ratio of BDE 197:201. The small value of this ratio (1.72, with values ranging from 28 to 35 in technical Octa- formulations) indicates that BDE 201 is produced due to photodebromination of BDE 209 in indoor dust.

In dust from 12 living rooms and garages of the same houses, as well as from the car (floor and seats) parked in the garage [18], BFR concentrations varied widely but systematically. Generally, concentrations were lower in vehicles, than in houses. Notable exceptions to that rule were BDEs 208, 207, 206, and especially BDE 209 in newer cars, which were sometimes an order of magnitude higher, indicating much more extensive use of the deca-formulation in vehicles. The elevated levels of BDE 209 in vehicles are consistent with the results of a research conducted in Greece [16] where median ΣBDE concentration of 200 pg/m^3 and a dominance of BDE 47, 99, and 209 was found.

An analysis using a method based on gas chromatography-mass spectrometry and pressurized liquid extraction has been performed on samples obtained from families and a research laboratory in Porto, Portugal [6]. The sampling process included 10 houses and parts (floors, seats and tailored car mats) of 9 car interiors. Sixteen PBDE congeners (BDE 28, 49, 47, 66, 100, 99, 85, 154, 153, 183, 197, 203, 196, 207, 206, and 209) were included in the analysis. PBDE concentrations did not differ in the sieved and whole fraction as it has been indicated by Mann Whitney U test. Lower BDE 209 levels (98 to 17,122 ng/g in sieved and 123 to 22,421 ng/g in whole car dust) compared to those detected in car dust from USA [19] and UK [20] (average 272,119 ng/g and 340,000 ng/g, respectively) have been found. These differences may be attributed to the car's characteristics (age, manufacturing etc.), the limited number of samples analysed, or the methodology of sampling. Sample collections in UK and USA studies were restricted to the surface of the seats. On the other hand the Portugal study included all the vacuum-cleaned parts of the car.

Thirty one people participated in a survey conducted in Boston in the winter of 2009. Their homes, offices and 20 cars had been sampled for PBDEs [21]. The cars were primarily manufactured abroad (2001 was the production year on the average). Dust samples from the entire surface of the front and back seats were analyzed using gas chromatography–mass spectrometry. The geometric means of concentrations in dust from the 20 cars were 2,950, 184, and 4,651 ng/g, for PentaBDE (sum of congeners 28/33, 47, 49, 66, 75, 85/155, 99, 100, 138, 153 and 154), OctaBDE (sum of BDEs 183, 196, 197, 201, 203) and BDE 209 (used for DecaBDE), respectively.

Dust samples from 13 cars, 7 homes, 4 offices, and 10 research laboratories collected in Kaohsiung City, Taiwan, were analyzed with a high-performance liquid chromatograph [22]. Dust samples from cars showed substantially higher (2,700 to 38,000 ng/g) BDE 209 concentrations.

2.1 Comparison of PBDEs found in vehicle cabin and trunk

Studies conducted in the passenger compartment of vehicles have indicated concentrations of volatile organic compounds declining over time, but increasing when the temperature reached higher values [23, 24, 25]. However, the factors influencing the levels of airborne PBDEs in

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vehicles or other indoor microenvironments remain poorly understood. The passenger cabin and the trunk are differently affected by dust due to its heterogeneous nature. Dust samples have shown that different parts in the cabin could be contaminated by a variety of fire retardant concentrations [12].

Passive samplers usually used to measure PBDE concentrations in car trunks may not collect suspended particulate matter and the measurements may represent the gas-phase concentrations only [26]. The concentrations of Σ(tetra-deca) BDEs in 21 cars [27] were monitored using a passive air sampler and they averaged 2,200 pg/m^3 in cabins and 1,600 pg/m^3 in trunks, respectively. In both the cabins and the trunks of the 21 cars, the atmospheric concentrations of Σ(tri-hexa) BDEs were statistically indistinguishable ($p>0.05$). On the opposite side, BDEs 206, 207, 208, and 209 concentrations in cabin air exceeded appreciably those in the trunk.

Increased in cabin use of fire retardants lead to elevated concentrations. Harrad and Abdallah [28] provided data from dust testing in 14 passenger cabins and trunks from cars in the United Kingdom assessing HBCDs, TBBP-A, along with 16 BDE congeners. They reported high concentrations of TBBP-A and of BDE 154, 206, 207, 208, and 209 in dust sampled in the front seats of the cars. Generally, concentrations in cabin dust exceeded significantly those in trunk dust ($p<0.05$). Nevertheless, in five cars, no significant differences ($p>0.05$) in concentrations of HBCDs and most PBDEs were detected in dust sampled from four different seating areas. Higher median levels of BDE 202 in cabin (14 ng/g) compared to trunk dust (0.3 ng/g) in the 14 vehicles have also been reported. BDE 202 is an octa-congener that has not been identified in any formulation in the market [29] and its detection speculates that the extent of BDE 209 photodecomposition is greater in the sunlit vehicle part (the passenger cabin) than in the dark vehicle part (trunk).

2.2 The role of vehicle's age in PBDEs concentration

As cars display the highest average concentrations of PBDEs, it is required to define relationships between PBDE concentrations and car age and manufacturer. The age of vehicles from 12 different manufacturers varied from 2 to 21 years [30]. No statistically significant relationship was found between log-normalized ΣBDE concentrations in the cars and the age. Omitting the two most contaminated cars, a significant ($p<0.01$) positive linear relationship was obtained. This finding indicates that the year of vehicle manufacture influences the PBDEs concentration in cars, but is not the only factor. The variation in concentrations is not solely attributable to vehicle age, but the quantity, age, and type of PBDE-containing goods in the car may also influence concentrations of PBDEs. This hypothesis has to be tested in a more detailed study required to characterize PBDE emission sources in vehicles.

The way the car of age affects ΣPBDE concentrations was imprinted in 33 vehicles studied by Mandalakis et al. [16] on 41 air samples from passenger space under normal driving conditions. ΣPBDE exhibited a gradual decrease from newer to older vehicles, not statistically significant due to the large variability of concentrations within each of the four defined age groups. Logarithmic concentration of ΣPBDE provided statistically significant correlation with vehicle age ($p<0.01$). The regression coefficient associated with vehicle age was negative and described the net reduction of PBDEs over time. Based on this value, the aforementioned authors estimated a half-life of 2.5 months for airborne ΣPBDE from private vehicles.

Dust from the seat surfaces of 66 personal automobiles in Villanova, Pennsylvania has been used in order to determine the concentration levels of 21 BDE congeners [31]. At the same time various features of the cars were recorded, including the vehicle manufacturer and model, the vehicle model year and the date of production (starting point for vehicle's age), the odometer reading (extent of vehicle use), the seat material, and the presence or absence of air conditioning, heated seats, a convertible top or a sunroof. Forty cars were manufactured after 2000, eight of which later than 2007. Individual PBDE congeners through bivariate correlations with vehicle age or the vehicle odometer reading didn't produce any significant Spearman correlations ($p > 0.05$).

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In order to characterize PBDE contamination in vehicle interiors, airborne concentrations of polybrominated diphenyl ethers were investigated using PUF disk passive air samplers fixed in 25 private cars for a period of 4 to 6 weeks [32]. Age of the vehicles was the most influential factor affecting polybrominated diphenyl ether emission in car interiors, though cars from the same manufacturer with similar ages have shown variations in PBDE concentrations.

3. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

The environment is hosting polybrominated diphenyl ethers released when they are produced, applied to consumer products or when the products containing them are discarded. There exists a general concern about PBDEs as they are persisting, bioaccumulative and with a high toxicity potential. Although production and use of PentaBDE and OctaBDE mixtures has been phased out, PBDE congeners will probably be present in the environment for many years. The assumption that DecaBDE in car interiors is breaking down into PentaBDE and other types of products highlights the need for actions for a prompt phase-out of its use. The progressive regulation of chemical additives in consumer products in Europe and end-of-life vehicle concerns in Asia is driving elimination of important chemical hazards from vehicles.

All reviewed studies demonstrate car interiors substantially contaminated with PBDEs; data from air samples showing appreciable contamination with PBDEs is consistent with information on PBDE contamination of windshield film and dust. The interior of new automobiles contain high levels of PBDEs on the basis of car furniture, like its floor coverings, arm rests, seat cushions and other plastic parts. The sampling in resale centers has shown similar congeners' concentrations leading to the conclusion that the car interior is their source. Measures to improve the indoor air of a car may include the use of solar reflectors, fans, air conditioning systems, or open windows. It is a good practice to park outside of sunlight whenever possible, since gas phase concentration of chemicals in parked vehicles approaches equilibrium relatively fast. This could be attributed to the large surface area of materials inside cars.

The contamination levels due to PBDE concentration in car dust are not homogeneous, since dust may not have its origin at components in the automobile's interior.

The hypothesis for the role of car age on the concentration of polybrominated diphenyl ethers has to be tested in a more detailed study required to characterize PBDE emission sources in vehicles.

An investigation is proposed to define potential differences in PBDEs concentrations inside idling or moving cars with the use of air cleaning devices and interior fan as a dependent variable.

References

[1] Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., Engelmann, W.H., 2001. The national human activity pattern survey (NHAPS): a resource for assessing exposure to environmental pollutants. *Journal of Exposure Analysis and Environmental Epidemiology*, **11(3)**, 231 – 252.

[2] Kalantzi, O.I., Siskos, P.A., 2011. Sources and human exposure to polybrominated diphenyl ethers. *Global NEST Journal*, **13(2)**, 99 – 108.

[3] WHO (World Health Organization) 1997. EHC-192 Environmental Health Criteria. Flame-retardants: a general introduction. *International Program on Chemical Safety*, Geneva, Switzerland.

[4] Alaee, M., Arias, P., Sjödin, A, Bergman, Å., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment International* **29(6)**, 683 – 689.

[5] Birnbaum, L.S., Staskal, D.F., 2004. Brominated Flame Retardants: cause for concern? *Environmental Health Perspectives*, **112(1)**, 9 – 17.

[6] Cunha, S.C., Kalachova, K., Pulkrabova, J., Fernandez, J.O., Oliveria, M.B.P.P., Alves, A., Hajslova, J., 2010. Polybrominated diphenyl ethers (PBDEs) contents in house and car dust of Portugal by pressurized liquid extraction (PLE) and gas chromatography–mass spectrometry (GC–MS). *Chemosphere*, **78(10)**, 1263 – 1271.

[7] The Ecology Centre, 2012. Guide to new vehicles Model Year 2011/2012. A Report. 43 p.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas

ISBN: 978-960-6865-94-7

[8] Webster, T.F., Harrad, S., Millette, J.R., Holbrook, R.D., Davis, J.M., Stapleton, H., Allen, J.G., McClean, M.D., Ibarra, C., Abdallah, A.-E., Covaci, A., 2009. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE209) in indoor environments using environmental forensic microscopy. *Environmental Science and Technology*, **43(9)**, 3067 – 3072.
[9] Gearhart, J., Posselt, H., 2006. Toxic at any speed: Chemicals in cars and the need for safe alternatives. The Ecology Centre: Ann Arbor, MI, USA, 1 – 32.
[10] Harrad, S., Wijesekera, R., Hunter, S., Halliwell, C., Baker, R., 2004. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environmental Science and Technology*, **38(8)**, 2345 – 2350.
[11] Wilford, B.H., Shoeib, M., Harner, T., Zhu, J., Jones, K.C., 2005. Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: implications for sources and exposure. *Environmental Science and Technology*, **39(18)**, 7027 – 7035.
[12] Harrad, S., Hazrati, S., Ibarra, C., 2006. Concentrations of polychlorinated biphenyls in indoor air and polybrominated diphenyl ethers in indoor air and dust in Birmingham, United Kingdom: Implications for human exposure. *Environmental Science and Technology*, **40(15)**, 4633 – 4638.
[13] de Wit, C.A., Thuresson, K., Björklund, J., 2008. Brominated flame retardants and perfluorinated compounds in air and dust from indoor environments in Stockholm. Institutionen för Tillämpad Miljövetenskap, Stockholms Universitet, 96 p.
[14] Thuresson, K., Björklund, J.A., de Wit, C.A., 2012. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm microenvironments 1: Levels and profiles. *Science of the Total Environment*, **414**, 713 – 721.
[15] Besis, A., Samara, C., 2012. Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments: A review on occurrence and human exposure. *Environmental Pollution*, **169**, 217 – 229.
[16] Mandalakis, M., Stephanou, E.G., Horii, Y., Kannan, K., 2008. Emerging contaminants in car interiors: evaluating the impact of airborne PBDEs and PBDD/Fs. *Environmental Science and Technology*, **42(17)**, 6431 – 6436.
[17] Abdallah, M.A., Harrad, S., Covaci, A., 2009. Isotope dilution method for determination of polybrominated diphenyl ethers using liquid chromatography coupled to negative ionization atmospheric pressure photoionization tandem mass spectrometry: validation and application to house dust. *Analytical Chemistry*, **81(17)**, 7460 – 7467.
[18] Batterman, S.A., Chernyak, S., Jia, C., Godwin, C., Charles, S., 2009. Concentrations and emissions of polybrominated diphenyl ethers from U.S. houses and garages. *Environmental Science and Technology*, **43(8)**, 2693 – 2700.
[19] Lagalante, A.F., Oswald, T.D., Calvosa, F.C., 2009. Polybrominated diphenyl ether (PBDE) levels in dust from previously owned automobiles at United States dealerships. *Environment International*, **35(3)**, 539 – 544.
[20] Harrad, S., Ibarra, C., Abdallah, M.A.-E., Boon, R., Neels, H., Covaci, A., 2008. Concentrations of brominated flame retardants in dust from United Kingdom cars, homes, and offices: causes of variability and implications for human exposure. *Environment International*, **34(8)**, 1170 – 1175.
[21] Watkins, D.J., McClean, M.D., Fraser, A.J., Weinberg, J., Stapleton, H.M., Sjödin, A., Webster, T.F., 2012. Impact of dust from multiple microenvironments and diet on pentaBDE body burden. *Environmental Science and Technology*, **46(2)**, 1192 – 1200.
[22] Huang, Y.-L., Wang, Y.-P., Yang, D.-R., Chen, S.-Y., Chen, J.-R., 2010. Assessment of Decabromodiphenyl Ether (BDE-209) in the indoor environment: Implications on environmental exposure assessment. *Proceedings BFR2010*, paper 90065, 4 p.
[23] Chien, Y.-C. , 2007. Variations in amounts and potential sources of volatile organic chemicals in new cars. *Science of the Total Environment*, **382(2-3)**, 228 – 239.
[24] Fedoruk, M.J., Kerger, B.D., 2003. Measurement of volatile organic compounds inside automobiles. *Journal of Exposure Analysis and Environmental Epidemiology*, **13(1)**, 31 – 41.
[25] Müller, D., Klingelhöfer, D., Uibel, S., Groneberg, D.A., 2011. Car indoor air pollution - analysis of potential sources. *Journal of Occupational Medicine and Toxicology*, **6(33),** 7 p.
[26] Wilford, B.H., Harner, T., Zhu, J., Shoeib, M., Jones, K.C., 2004. A passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada. *Environmental Science and Technology*, **38(20)**, 5312 – 5318.
[27] Abdallah, M.A.-E., Harrad, S., 2010. Modification and calibration of a passive air sampler for monitoring vapor and particulate phase brominated flame retardants in indoor air: application to car interiors. *Environmental Science and Technology*, 44**(8)**, 3059 – 3065.
[28] Harrad, S., Abdallah, M.A., 2011. Brominated flame retardants in dust from UK cars—within vehicle spatial variability, evidence for degradation and exposure implications. *Chemosphere*, **82(9)**, 1240 – 1245.
[29] Law, R.J., Herzke, D., Harrad, S., Morris, S., Bersuder, P., Allchin, C.R., 2008. Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. *Chemosphere*, **73(2)**, 223 – 241.

ISBN: 978-960-6865-94-7

[30] Hazrati, S., Harrad, S., 2006. Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air. *Environmental Science and Technology*, **40(24)**, 7584 – 7589.
[31] Lagalante, A.F., Shedden, C.S., Greenbacker, P.W., 2011. Levels of polybrominated diphenyl ethers (PBDEs) in dust from personal automobiles in conjunction with studies on the photochemical degradation of decabromodiphenyl ether (BDE-209). *Environment International*, **37(5)**, 899 – 906.
[32] Hazrati, S. Harrad, S., Alighadri, M., Sadeghi, H., Mokharti, A., Gharari, N., Rahimzadeh, S., 2010. Passive air sampling survey of polybrominated diphenyl ether in private cars: implications for sources and human exposure. *Iranian Journal of Environmental Health Science and Engineering*, **7(2)**, 157 – 164.

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Innovative Technologies for Polluted Water Remediation

PROTECTION
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Discontinuous permeable adsorptive barrier design and cost analysis: a methodological approach to optimisation

G. F. Santonastaso[1], I. Bortone[2], S. Chianese[1*], A. Di Nardo[1], M. Di Natale[1], A. Erto[3], D. Musmarra[1], D. Karatza[1]

[1] Seconda Università degli Studi di Napoli, Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, via Roma 29, 81031, Aversa (CE), Italy.
[2] London South Bank University, School of Engineering, 103 Borough Road, SE1 0AA, London UK.
[3] Università degli Studi di Napoli Federico II, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio, 80, 80125, Napoli, Italy.
*Corresponding author: Email: simeone.chianese@unina2.it

Abstract

A methodological approach for the optimisation of a Discontinuous Permeable Adsorptive Barrier (PAB-D) is proposed in this paper. This method is based on the comparison of different PAB-D configurations, obtained by varying some of the main PAB-D design parameters. In particular, the well diameters, the distance between two consecutive passive wells and the distance between two consecutive well columns are varied and a cost analysis for each configuration is carried out in order to define the most performing and cost-effective well outline. As case study, a benzene contaminated aquifer located in an urban area in the north of Naples (Italy) is considered. Moreover, a comparison with a Continuous PAB (PAB-C) is made so to define the best configuration for the case-study.

Keywords: *discontinuous permeable adsorptive barrier; benzene; groundwater remediation; design and cost analysis; optimisation.*

1. INTRODUCTION

Groundwater is a fundamental water supply for drinking, agricultural and industrial uses. A proper management of this important natural resource is essential and can be achieved via prevention and protection of groundwater quality from pollution. An innovative and flexible *in-situ* technology, able to protect and remediate aquifers from different types of contaminants, e.g. heavy metals [1] and organic compounds [2,3], is Permeable Reactive Barriers (PRBs) [4]. PRBs are a passive and cost-effective decontamination technique and consist of a vertical wall crossing the polluted aquifer. Clogging phenomena are the main disadvantage of PRBs [5,6]. A reactive medium, which is more permeable than the surrounding aquifer, is used to fill the whole barrier in order to boost groundwater flow through it exploiting the aquifer natural gradient [2,4]. If an adsorbing material is adopted as barrier filler, PRBs can be defined Permeable Adsorptive Barriers (PABs) and the groundwater remediation occurs by adsorption. In their typical configuration, PABs are a continuous wall (PAB-C); however, several innovative configurations such as Discontinuous Permeable Adsorptive Barriers (PABs-D) have been proposed during last few years [7,8]. A PAB-D consists in a passive well array set in one or more columns at a defined distance one another and filled with adsorbing materials. Such a configuration is more advanced than PAB-C as it allows the remediation of the same volume of groundwater with a smaller barrier volume and consequently at a lower cost [9].

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This paper deals with a methodological approach for PAB-D optimisation, applied to an aquifer located north of Naples (Italy), already adopted as case-study in previous published papers [2,8-10]. In this site, analytical data deriving from dedicated measurement campaigns showed the presence of both organic and inorganic pollutants. In particular, benzene, which is listed among the priority contaminants by U.S. EPA as carcinogenic [11,12], was found at a concentration higher than the Italian regulatory limit (C_{lim}=1 µg L^{-1})set for groundwater quality. The proposed approach is based on the definition of a set of several PAB-D configurations, all allowing the interception and treatment of the entire contaminated groundwater, and on the combination of an optimal design technique and cost analysis, aiming at minimizing the remediation costs. The optimisation was carried out by varying the well diameter and assuming both the distance between two consecutive wells and the distance between two consecutive well lines as a function of the diameter. Remediation costs were calculated as the sum of the well drilling costs and the adsorbing material costs, also including the monitoring costs of the installation. Moreover, a comparison between a Continuous PAB (PAB-C), already designed for the remediation of the same site [10], and the optimal PAB-D was carried out.

2. MATERIALS AND METHODS

2.1 Process modelling

The time evolution of pollutant species in groundwater in presence of adsorbing phenomena can be described via the advection-dispersion-reaction equation (Equation 1), which can be written as follows [2,13]:

$$\frac{\partial C}{\partial t} = \nabla\left(D_h \nabla C\right) - \frac{\vec{u}\nabla C}{n_S} - \frac{\rho_b}{n_b}\frac{\partial \omega}{\partial t} \tag{1}$$

where C is the groundwater contaminant concentration, t is the time, D_h is the hydrodynamic dispersion tensor, $\vec{u}$ is the water flow rate, n_s is the site porosity, ρ_b is the adsorbing material bulk density, n_b is the barrier porosity and ω is the pollutant concentration on the adsorbent (i.e. its adsorption capacity). The hydrodynamic dispersion tensor, D_h , is expressed as the sum of the tensor of mechanical dispersion, D_m, and the coefficient of molecular diffusion, D_{iff}, (a scalar), as better described by Konikow and Grove [14]. Darcy equation (Equation 2) can be used to evaluate the water flow rate $\vec{u}$ as:

$$\vec{u} = K_S \cdot \nabla h \tag{2}$$

In Equation 2, K_s is the hydraulic conductivity and h is the hydraulic head. The last term on the right side of Equation (1) accounts for PAB adsorption phenomena and can be defined by the following equation:

$$-\frac{\rho_b}{n_b}\frac{\partial \omega}{\partial t} = k_c a\left[C - C^*(\omega)\right] \tag{3}$$

where k_c is the mass transfer coefficient for adsorption reaction, a is the adsorbent particle external specific surface area and $C^*(\omega)$ is the pollutant concentration in the liquid phase at thermodynamic equilibrium with the concentration on the adsorbent (ω). The thermodynamic equilibrium is usually expressed through an adsorption isotherm, such as the Langmuir model (Equation 4):

$$\omega = \frac{\omega_{\max} K C^*(\omega)}{1 + K C^*(\omega)} \tag{4}$$

where ω_{max} and K are the Langmuir parameter. The computational domain was defined by considering a 2D system assuming constant concentrations of benzene along the vertical groundwater direction and with the reference border coinciding with the boundary of the site domain. Moreover, an initial concentration of benzene onto the adsorbing material of the PAB equal

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to zero and a constant porosity in all computational domain were assumed. The following initial and boundary conditions were used:

$$C = 0 \quad \begin{cases} x = 0 & \forall y \forall t \\ y = 0 & \forall x \forall t \\ y = Y & \forall x \forall t \end{cases} \tag{5}$$

$$\frac{\partial C}{\partial t} + \bar{u}\nabla C - \nabla(D_h \nabla C) = 0 \quad x = X \quad \forall y \forall t$$

X and Y were assumed as coincident with the size of the computational domain, in the x- and y-directions, respectively. A finite element method was applied to numerically solve the equation system (1)-(4), with the related initial and boundary conditions (5), in COMSOL Multi-physics® environment.

2.2 PAB-D optimization approach

The drilling of PABs may be a complex task for deep aquifers and the use of adsorptive passive wells (i.e. a PAB-D) can be more appropriate and easier to implement with respect to a PAB-C. Moreover, if a PAB-D is properly designed and strategically placed in the polluted site it can result also as very cost-effective. In order to minimise PAB-D dimensions and consequently the remediation costs, a methodological approach to optimize PAB-Ds is proposed in the following. The approach is based on the definition of a set of several PAB-D configurations that allow the treatment of the whole polluted aquifer, based on the combination of an optimal design technique previously proposed by the authors [9] and a cost analysis for each passive well array layout. As described elsewhere [2,8-10], the design of a Permeable Adsorptive Barrier requires a preliminary field investigation of the considered area in order to know its hydrogeological characteristics, groundwater hydraulic heads and direction, as well as the location, nature and extent of the site contamination. A proper PAB-D design is aimed at defining the geometric configuration of the passive well array, which is able to intercept the whole contaminant plume and decontaminate the groundwater. The PAB-D geometric parameters are shown in Figure 1 and in particular they are: the passive well geometrical parameters (diameter (D_w) and height (H)), the distance between two consecutive passive wells (I) along a line, the number of well lines (n_c) of the array, the line-to-line distance (d_c), the orientation (ε) and the well-barrier position [8,9]. Moreover, an appropriate adsorbing material has to be used. By varying one of these parameters, such as D_w, I or d_c, a different PAB-D configuration is obtained. In each configuration, the height of wells (H) can be kept as constant and equal to the aquifer thickness. A 2D system with constant concentrations of benzene along the groundwater vertical direction is assumed; moreover, a well grid is defined so as to put each well line orthogonal to the groundwater flow direction and as close as possible to the contaminated plume [2].

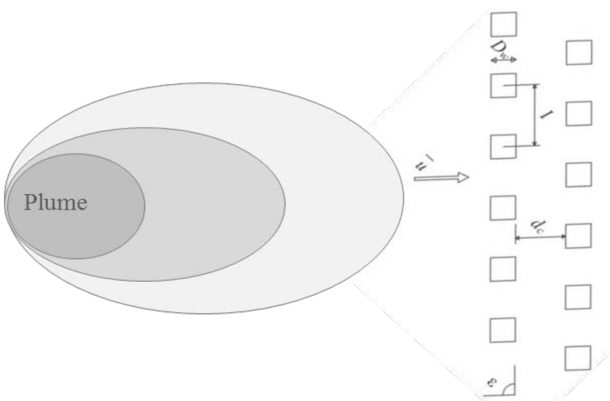


Figure 1. Design parameters of a PAB-D [7]

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Each PAB-D configuration was determined by varying the well diameter (D_w) and assuming both the distance between two consecutive passive wells (I) and the line-to-line distance (d_c) a function of D_w. In this way, the variation of number of wells (n_w) for each line also occurred. In particular, according to the optimal design technique adopted, for each configuration, D_w, I and d_c were kept constant while the number of wells (n_w) and the number of lines of the array (n_c) were varied up to determine the configuration with a minimum total number of wells and, consequently, minimum amount of adsorbing material. A heuristic method was used to put into practice the optimal design technique [15]. In addition, a cost analysis was made to assess the remediation costs (C_R) of each configuration. Only PAB-D drilling costs (C_{well}) and monitoring costs (C_M) were considered, while operation and maintenance costs were excluded since PABs are a passive remediation technique, as they do not need energy consumption and workers. Finally, PAB-D costs were determined as the sum of the well and adsorbing material (C_{Ad}) costs:

$$C_R = C_{well} + C_{Ad} + C_M \tag{6}$$

The methodological approach was finalized to identify the PAB-D configuration among that of the set with the lowest remediation costs, according to the following objective function (O.F.):

$$O.F. = \min\left[C_R\left(D_w, I, d_c\right)\right] \tag{7}$$

3. CASE STUDY

The PAB-D optimization method was applied to the remediation of a groundwater in the surroundings of an urban area located north of Naples (Italy). The area of study has an extent of 225 ha and several solid waste landfills are still present around.. The underlying aquifer (40 m depth from the soil surface) has an average thickness of 8 m and is confined by an impermeable layer. Groundwater soil composition was schematized as a single layer consisting in Neapolitan yellow tuff with hydraulic conductivity (K_S) and longitudinal dispersivity (α_x) equal to 5×10^{-5} m s^{-1} and 1 m, respectively. The equation proposed by Gelhar et al. [16] was used to estimate transverse dispersivity (α_y):

$$\alpha_y = \alpha_x / 10 \tag{8}$$

Several contaminants, both inorganic and organic, were found in groundwater. Among them, benzene was detected at concentrations up to 6 times higher than the corresponding Italian regulatory limit for groundwater quality (C_{lim}=1 µg L^{-1}).In Figure 2, the benzene initial concentrations and the groundwater piezometric heads and direction are sketched. The contaminant plume extends for an area of about 500 m x 450 m; the aquifer is east-west oriented with piezometric levels from 12 to 7 m, under a gradient (J) of 0.01 m m^{-1}.

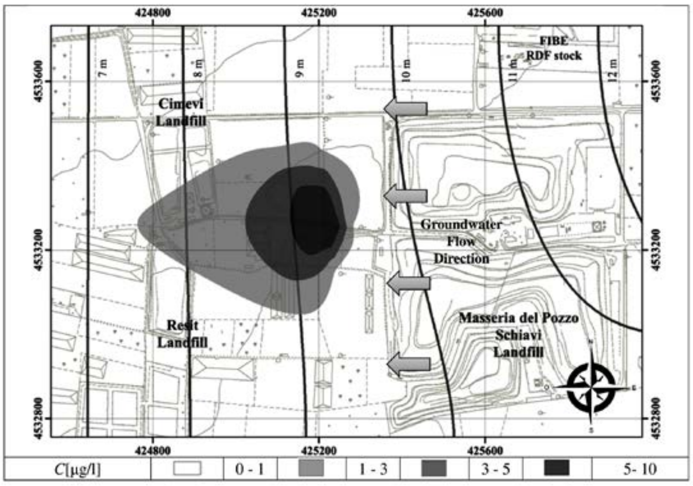


Figure 2.
Benzene iso-concentrations and groundwater piezometry of the area of investigation

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The main characteristics of the aquifer, including the molecular diffusion coefficient of benzene, are collected in Table 1.

Table 1. Main characteristics of the case-study area

Aquifer characteristic	
Total extent, A [ha]	225
Aquifer average piezometric level, H_w [m]	8
Piezometric gradient, J [m m^{-1}]	0.01
Porosity, n_s [-]	0.25
Dry soil bulk density, ρ_s [kg m^{-3}]	1400
Hydraulic conductivity, K_s [m s^{-1}]	5×10^{-5}
Longitudinal dispersivity, α_x [m]	1
Transverse dispersivity, α_y [m]	0.1
Molecular diffusion coefficient, D_{iff} [m^2 s^{-1}]	10^{-8}

Adsorption modelling was carried out by considering as adsorptive material an activated carbon tested by Basso and Cukierman [17]. Benzene adsorption isotherm is described by the Langmuir model, expressed by Eq. (4), with ω_{max} and K equal to 35.1 mg g^{-1} and 0.0577 L mg^{-1}, respectively [17]. The main characteristics of the adsorbing material are collected in Table 2. The optimization approach was applied to a set of several PAB-D configurations, which were defined by varying the well diameters (D_w) in the range 0.4-1.2 m, while the distance between two consecutive passive wells (I) and the line-to-line distance (d_c) were set equal to twice the diameter and equal to the diameter, respectively. The set of configurations tested is summarised in Table 3.

Table 2. Main characteristics of the adsorbing material

Adsorbing material characteristics	
Porosity, n_b [-]	0.45
ACs bulk density, ρ_b [kg m^{-3}]	520
Hydraulic conductivity, K_{PAB} [m s^{-1}]	10^{-3}
Longitudinal dispersivity, α_{xPAB} [m]	0.05
Transverse dispersivity, α_{yPAB} [m]	0.005
AC BET surface area, S_{bet} [m^2 g^{-1}]	1.116
AC average pore diameter, d_{pore} [nm]	233.5

Table 3. Defined configuration for the optimization approach

#	D_w [m]	$I = 2*D_w$ [m]	$d_c = D_w$ [m]
1	0.4	0.8	0.4
2	0.5	1.0	0.5
3	0.6	1.2	0.6
4	0.8	1.6	0.8
5	1.0	2.0	1.0
6	1.2	2.4	1.2

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Table 4. PAB-D costs

C_{well}		C_{Ad}	C_M
D_w [m]	**Unit cost [€ m^{-1}]**	**Unit cost [€/m$^3_{Ad}$]**	**[€]**
0.4	47	780	250000
0.5	51		
0.6	57		
0.8	69		
1.0	87		
1.2	103		

The cost analysis was performed by considering the well drilling costs (C_{well}), the adsorbing material cost (C_{Ad}) and the monitoring costs (C_M). The well drilling costs depend on both diameter and number of wells. The larger the well diameter the higher the well drilling unit cost, expressed per unit of perforation depth; moreover, it depends on the geological soil composition. The adsorbing material unit cost, expressed for unit of volume, and the monitoring costs were assumed as constant for all the PAB-D configurations (Table 4).

4. RESULTS AND DISCUSSION

The amount of adsorbing material volume (V_{Ad}) and the cost analysis for each PAB-D configuration are listed in Table 5. PAB-D layouts required 2 passive well lines (n_c=2) for Configurations 1-3 while a single passive well line was required for Configurations 4-6. It was observed that the number of wells (n_w) decreased by increasing the well diameter, and, in particular, by reducing the well lines from 2 to 1, a significant reduction of about 50% was obtained. V_{Ad}, calculated by considering a constant aquifer height (H=8 m), increases with the well diameter at constant number of well lines and the minimum value was found when 1 line is adopted and in correspondence of D_w=0.8 m.

The remediation costs (C_R) reported in Table 5 and depicted in Figure 3. As shown in Figure 3, C_{Ad} increases almost monothonically with well diameter (which in turn influences the number of well lines requested), while C_{well} follows an opposite trend because a smaller number of wells is needed (Table 5), despite their higher unit costs (Table 4). In particular, C_{well} resulted higher than C_{Ad} for the first 3 configurations with 2 passive well lines, while the opposite trend can be observed for the last 3 with a single passive well line. Moreover, a higher incidence of the C_{Ad} on total costs C_R by increasing the wells diameter can be observed, becoming higher than 50% with configurations with 1 line. Since the monitoring costs (C_M) were considered equal to 250000€ for all configurations, the minimum of C_R occurs when the increase of C_{Ad} and the decrease of C_{well} compensate.

Table 5. Results of the methodological approach to PAB-D optimisation

#	D_w [m]	H [m]	n_c	n_w	V_{Ad} [m^3]	C_{well} [€]	C_{Ad} [€]	C_R [€]	Incidence of C_{Ad} on C_R [%]
1	0.4	8	2	788	126	1626432	786739	2663171	30
2	0.5	8	2	610	153	1376160	951600	2577760	37
3	0.6	8	2	540	194	1321920	1213056	2784976	44
4	0.8	8	1	257	164	703152	1026355	1979507	52
5	1.0	8	1	205	205	678960	1279200	2208160	58
6	1.2	8	1	158	228	659808	1419725	2329533	61

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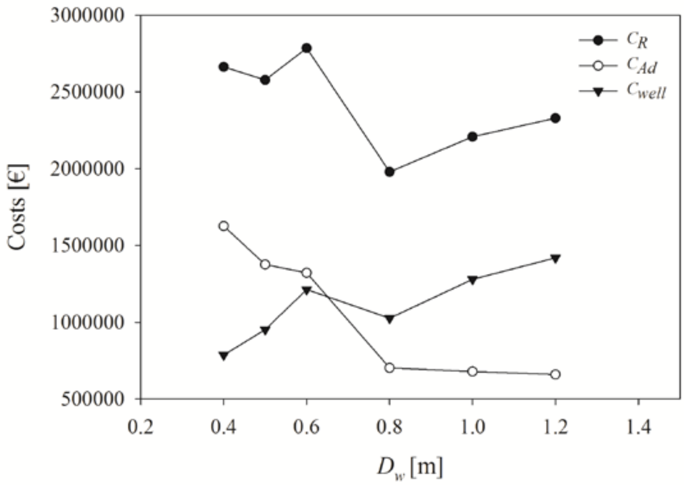


Figure 3. Costs trend as a function of the well diameter

In fact, the lowest remediation cost C_R was obtained for the configuration 4, i.e. with well diameter equal to 0.8m, which also experienced the highest reduction in C_{Ad} (Figure 3).

In Figure 4, for the best PAB-D configuration (i.e. number 4 – D_w=0.8 m), the maximum benzene concentration at the inlet and at the outlet of the barrier were represented as breakthrough curves. As shown, an operating time close to 20 years is required to capture the whole polluted plume and to remediate the aquifer. Moreover, the PAB-D efficiency was tested up to 100 years of working time in order to verify the absence of benzene desorption from the barrier at concentrations higher than the Italian regulatory limit (C_{lim}=1 µg L^{-1}) [16]. As depicted, for the whole simulated operating time, the outlet benzene concentrations were lower than 1 µg L^{-1}.

Finally, a comparison between a Continuous PAB (PAB-C) [9], designed for the remediation of the same site, and the optimised PAB-D was carried out. The values of both PAB-C and PAB-D parameters are listed in Table 6, where the corresponding total adsorbing material volume and remediation costs were also reported. The optimised PAB-D allows a reduction of the adsorbing material volume (ΔV_{ad}) and remediation costs (ΔC_R) equal to 28% and 40%, respectively.

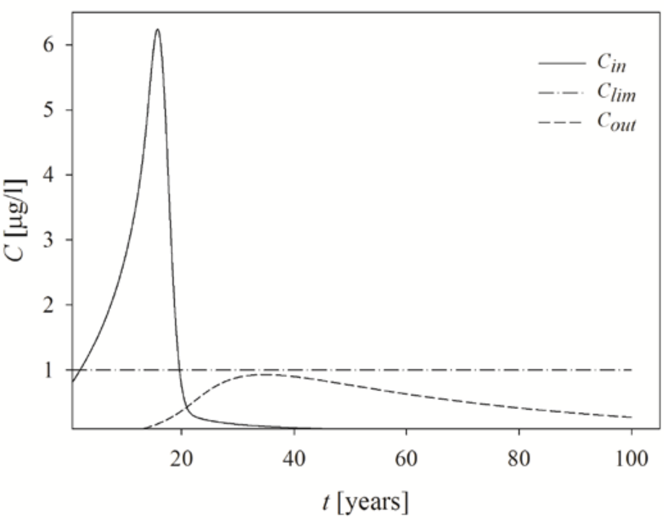


Figure 4. Breakthrough curves for the Optimised PAB-D

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Table 6. Comparison between Continuous and optimised Discontinuous PAB

	Height [m]	Width [m]	Length [m]	V_{ad} [m^3]	ΔV_{ad} [%]	C_R [€]	ΔC_R [%]
PAB-C	8	0.57	400	1824		3304720	
Optimised PAB-D	8	0.8	257 x 0.8	1316	28	1979507	40

5. CONCLUSIONS

In this paper, a methodological approach for PAB-D optimisation was proposed. The method was based on the definition of a set of several PAB-D configurations, all allowing to intercept the contaminated plume and to remediate the groundwater, and on the combination of an optimal design technique and a cost analysis for each of the configurations considered. The set of PAB-D configurations was determined by varying the well diameter (D_w) and assuming both the distance between two consecutive passive wells (I) and the line-to-line distance (d_c) as a function of D_w. The methodological approach was finalized to identify the PAB-D configuration with the lowest remediation costs. This latter were calculated as the sum of well drilling costs, adsorbing material costs and PAB-D monitoring costs. Results showed that a lower amount of adsorbing material was obtained by reducing the number of the PAB-D wells and the configuration with D_w=0.8 m, I=1.6 m and d_c=0.8 m resulted to be the optimised PAB-D layout since the remediation costs were the lowest among the configurations tested.

Finally, a comparison between a Continuous PAB and the optimised PAB-D, applied on the same site, showed that the optimised PAB-D determines a 28% and 40% reduction of adsorbing material volume and remediation costs, respectively.

References

[1] Park, T.Y., Shin, W.S., Choi S., 2012. Sorptive removal of cobalt, strontium and cesium onto manganese and iron oxide-coated montmorillonite from groundwater. *Journal of Radioanalytical and Nuclear Chemistry*, **292**, 837-852.

[2] Erto, A., Lancia A., Bortone I., Di Nardo A., Di Natale, M., Musmarra D., 2011. A procedure to design a Permeable Adsorptive Barrier (PAB) for contaminated groundwater remediation. *Journal of Environmental Management*, **92**, 23-30.

[3] Erto, A., Bortone, I., Di Nardo, A., Di Natale, M., Musmarra, D., 2014. Permeable Adsorptive Barrier (PAB) for the remediation of groundwater simultaneously contaminated by some chlorinated organic compounds. *Journal of Environmental Management*, **140**, 111-119.

[4] U.S. EPA, 1999. *Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers*, EPA, 542-R-99-002.

[5] Prisciandaro, M, Lancia, A., Musmarra, D, 2001. Calcium sulfate dihydrate nucleation in the presence of calcium and sodium chloride salts. *Industrial and Engineering Chemistry Research*, **40(10)**, 2335-2339.

[6] Prisciandaro, M., Lancia, A., Musmarra, D., 2003. The Retarding Effect of Citric Acid on Calcium Sulfate Nucleation Kinetics. *Industrial and Engineering Chemistry Research*, **42(25)**, 6647-6652.

[7] Wilson, R.D., Mackay, D.M., Cherry J.A., 1997. Arrays of unpumped wells for plume migration control by semi-passive in situ remediation. *Groundwater Monitoring & Remediation*, **17**, 185–193.

[8] Bortone, I., Di Nardo, A., Di Natale, M., Erto, A., Musmarra, D., Santonastaso, G.F., 2013. Remediation of an aquifer polluted with dissolved tetrachloroethylene by an array of wells filled with activated carbon. *Journal of Hazardous Materials*, **260**, 914–920.

[9] Santonastaso, G. F., Bortone, I., Chianese, S., Erto, A., Di Nardo, A., Di Natale, M., Musmarra, D., 2015. Application of a discontinuous permeable adsorptive barrier for aquifer remediation. A comparison with a continuous adsorptive barrier. *Desalination and Water Treatment*, doi: 10.1080/19443994.2015.1130921.

[10] Bortone, I., Erto, A., Santonastaso, G., Di Nardo, A., Di Natale, M., Musmarra, D., 2015. Design of Permeable Adsorptive Barriers (PABs) for groundwater remediation by COMSOL Multi-physics simulations. *Desalination and Water Treatment*, **55(2)**, 3231-3240.

ISBN: 978-960-6865-94-7

[11] Staples, C.A., Werner, A.F., Hoogheem, T.J., 1985. Assessment of priority pollutant concentrations in the United States using storet database. Environmental Toxicology & Chemistry, **4**, 131–142.

[12] World Health Organization, 1993. *Benzene, Environmental Health Criteria 150*.

[13] Bear, J., 1979. *Hydraulics of Groundwater*, McGraw-Hill, New York.

[14] Konikow, L.F., Grove, D.B., 1977. *Derivation of equations describing solute transport in ground water*. US Geological Survey, Water-Resources Investigations Report 77-19.

[15] Di Nardo, A., Bortone, I., Di Natale, M., Erto, E., Musmarra, D., 2014. A heuristic procedure to optimize the design of a permeable reactive barrier for in situ groundwater remediation. *Adsorption Science & Technology*, **32**, 125-140.

[16] Gelhar, L.W., Welty, C., Rehfeldt, K.R., 1992. A critical review of data on field-scale dispersion in aquifers. *Water Resources Research*, **28**, 1955–1974.

[17] Basso, M.C. and Cukierman, A.L., 2005. Arundo donax-Based activated carbons for aqueous-phase adsorption of volatile organic compounds. *Industrial and Engineering Chemistry Research*, **44**, 2091-2100.

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Purification of residual leach liquors from hydrometallurgical process of NiMH spent batteries through Micellar Enhanced Ultra Filtration

V. Innocenzi, F. Tortora, M. Prisciandaro*, F. Vegliò

University of L'Aquila, Dept. of Industrial and Information Engineering and of Economics
Viale Giovanni Gronchi 18, 67100 L'Aquila Italy.
*Corresponding author: Email: marina.prisciandaro@univaq.it

Abstract

Hydrometallurgical processes for the treatment and recovery of metals from waste electrical and electronic equipment produce a lot of wastewaters containing heavy metals. To become a sustainable process, such operations should be developed in order to maximize the recovery of the metals of interest and minimize the amount of wastes and wastewaters produced. The research activity presented in this paper is focused on the use of ultrafiltration combined with surfactant micelles (micellar-enhanced ultrafiltration, MEUF) for purification of leach liquors obtained after leaching of NiMH spent batteries. The experiments are carried out in a lab-scale plant, where a tubular ceramic ultrafiltration membrane is used with adding a surfactant to concentrate heavy metals in the retentate stream, producing a permeate of purified water that can be reused inside the process, thus minimizing the fresh water consumption.

Keywords: NiMH spent batteries; wastewaters; heavy metals; MEUF; water reuse

1. INTRODUCTION

The batteries are devices that convert chemical in electrical energy. These are divided in two main categories: the primary and secondary cells. In the first ones the internal chemical reactions are irreversible. In other words when all reagents are completely transformed in the final products, the cells are discharge and become unusable. Zinc-carbon, alkaline, silver, lithium are examples of primary cells. The second kind of batteries are therechargeable cells whose charge can be completely reestablished by the application of an appropriate electrical energy. There are several types with different electrical proprieties, chemical compositions and dimensions. Examples of them are: acid-lead, Lithium ions, nickel –cadmium (NiCd), zinc-nickel and nickel-metal-hydride batteries (NiMH).

Every year around 800.000 tons of automotive batteries, 190.000 tons of industrial batteries and 160.000 tons of portable cells (30% of rechargeable) are market in the European Union [1].

All batteries contain a series of dangerous metals, acid and basic solutions that cannot be released into the environment at the end of their useful life. For example the lead batteries are considered at high toxicity due at the presence of lead and sulfuric acid. For these reasons the spent batteries are classified as dangerous waste, Directive 2006/66/EC and Directive 2008/103/EC [2,3]. These directives encourage the European States to increase the waste collection and the recycle. In particular the directives requires the following targets to be achieved: 45% collection rate for waste portable batteries to be met by September 2016; 100% collection and recycling target with the prohibition on the disposal by landfill or incineration of waste industrial and automotive batteries; and 65% of lead acid batteries,**75%** of nickel-cadmium batteries and **50%** of other waste batteries

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is recycled. Eurostat provides a series of data related to 2013 that show Belgium, Luxembourg, Sweden and Austria are the most virtuous European countries with a ratio from collected spent batteries and market batteries of more than 50%, Portugal, Poland and Latvia with less than 30% [4]. As regards Italy, 31.8% of batteries and accumulators has been properly collected in 2013, 4% more than in 2012 [5].In the sector of the production of hybrid cars lead-acid, NiMH are Li-ion batteries are used. The first type is destined to disappear for the presence of dangerous materials and in part because reduce the efficiency of the car. NiMH batteries contain 36-42% of Ni, 3-4% Co and 8-10% of rare earths (La, Ce, Pr and Nd) [6].The Li-ion batteries have a negative electrode in graphite while the positive one is a metallic oxides($LiCoO_2$, $LiFePO_4$ or $LiMn2O_4$) and the electrolyte is a lithium salt in an organic solvent. The several materials of the batteries influence the performance, the cost and the environmental impact. The number of production of hybrid cars will increase in the future, for example in the United Kingdom 32.715 (20,5% more than in 2012) were sold in the 2013, 7600 in Germany 2013 [7]. In Italy more than 14.800 cars were sold in 2014, more than 30% respect to 2013 [8]. The sale of this type of machines is still a market niche compared to the traditional machines but already in these years recycling processes of the spent batteries are studying to reduce their environmental impact, for recovering metals such as nickel, manganese, and recover the critical materials such as graphite and rare earths (lanthanum, cerium, praseodymium). The recycling treatments can be classified as pyrometallurgical and hydrometal-lurgical processes. The second one consists of material dissolution using reagents (acids or base) and recovery of dissolved metals by selective precipitation, solvent extraction, crystallization and others chemical operations. The hydrometallurgical treatment could be more or less complex and depends on the initial material and on the elements to recover. Pyrometallurgical processes consist of recovering materials using furnaces that work high temperatures. A number of companies around the world treat spent batteries and the most of them use conventional pyrometallurgical processing techniques to produce metals for re-alloying during the production of commercial metals. .The majority of existing hydrometallurgical processes for the treatment of spent NIMH batteries include a leaching stage, where the battery content is treated with a sulphuric solution [9, 10, 11, 12, 13, 14, 15, 16, 17] or using HCl solution [19, 20, 21, 22].These studies have demonstrated that it is possible to obtain the quantitative dissolution of metals and rare earths. After dissolution rare earths can be selectively recovered by precipitation as double sulfate salts [10, 13, 14, 16, 22, 23] or processed by solvent extraction, precipitation and recovered as rare earth's oxides [17, 18]. The previous works showed that after rare earths precipitation other metals, mainly zinc, manganese, cobalt and nickel remained in the solutions. The residual liquors need to be treated for the removal of these metals. The activities introduce in the present paper are just focused on the treatment of purification of the residual solutions coming from NiMH spent process. The present paper describes in detail the experimental tests carried out on pregnant solutions simulating the leach liquors of NiMH spent batteries to separate base metals after rare earths precipitation. The aim is to verify if the MEUF technique, successfully employed in other polluted liquid wastes treatment [24, 25, 26], is able for treating the residual leaching solution containing Ni, Mn and Zn. The experiments are carried out in a lab-scale plant, where a tubular ceramic ultrafiltration membrane is used with adding a surfactant to concentrate heavy metals in the retentate stream, producing a permeate of purified water that can be reused inside the process, thus minimizing the fresh water consumption. The novelty of this study is relative to the use of MEUF integrated in a hydrometallurgical process for the recovery of metals from NiMH spent batteries. The results of the experiments showed that MEUF is a valuable method to recover base metals from residual solution coming from rare earths recovery step.

2. MATERIALS AND METHODS

2.1. Apparatus description

Experimental studies have been carried out in a tangential flow Membralox® XLAB 3 (Exekia, Bazet, France) laboratory pilot plant with a single tube Membralox® Tl-70 ceramic ultrafiltration membrane (Fig. 1). The recirculation pump gives a fixed tangential velocity of about 7 m/s. All experiments were performed at room temperature; for the cleaning procedure, in which water was at 40°C, temperature was controlled by the tank jacket connected to a Crioterm 10–80 thermostatic bath. The plant is equipped with a backflush system BF3, controlled by an electrovalve (pressure7 bar, re-injected volume 3 ml). Backflush was utilized only during membrane cleaning, with intervals and lengths regulated manually (frequency 2 min, length 1 s, approximately). The pore size of membranes used in experimental work was 210 KDa.

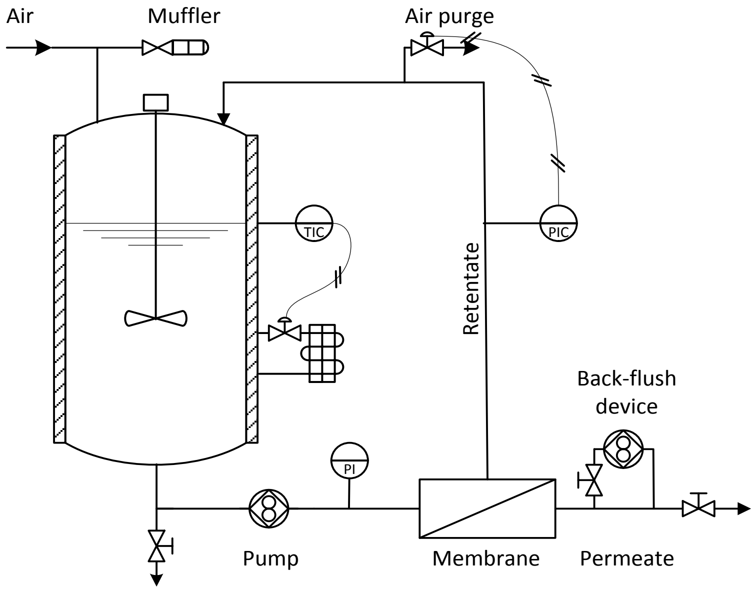


Figure 1. Sketch of the experimental apparatus

2.2. Feed water characteristics

Wastewater utilized in this study was a synthetic liquid solution. In details, distilled water was produced by a D10-T distiller (Enrico Bruno Company), and depending on the solution to be tested, manganese, nickel, zinc and then sodium dodecyl sulfate (SDS) as surfactant. Sodium dodecyl sulfate (SDS) of Merck Millipore was used as a surfactant (Molecular mass 288.38 g/mol), manganese (II) sulfate monohydrate (Molecular mass 169.02 g/mol) (Sigma Aldrich), zinc sulfate monohydrate (Molecular mass 179.45 g/mol) (Fluka), and a nickel (II) sulfate-hexa-/heptahydrate (Molecular mass 154.76 g/mol) (Riedel-de Haen) were the metals salt used in the sample preparation. The critical micellar concentration (CMC) of SDS at 25 °C is 6 to 8mMand for the calculations of the concentration of SDS under CMC we considered 4 mM that correspond to a concentration of 1.15 mg/L and 4.025 g of SDS for 3.5 L of solution while for the calculations of the concentration of SDS above CMC we considered 10 mM that correspond to a concentration of 2.88 mg/L and10.08 g of SDS for 3.5 L of solution. The concentration of metals are 9.86 mg/L Zn, 18 mg/L of Mn, 7.33 mg/L of Ni respectively.

2.3. Ultrafiltration procedure

Table 1 shows the experiments carried out for removal of metals as zinc, manganese and nickel from a synthetic solutions that simulated the residual liquors coming from a hydrometallurgical

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process for the treatment of NiMH spent batteries [16,23]. The rejection yields of the metals were studied as a function of SDS concentration and pressure using a membrane with 210 KDa.

Table 1. Experimental plan (tubular ceramic membrane 210 kDa)

Test	SDS concentration [mg/L]	Pressure [bar]
1	0	0.8
2	0	2.8
3	x2	0,8
4	x2	2.8
5	x1	1.3

The tests were performed at different values of pressure [0.8 and 2.8 bar] and SDS concentration [without and with surfactant at concentration greater than CMC, X2]. Moreover another test was carried out at average operating conditions than those listed, in particular using a concentration of SDS equal to X1 (under CMC) and 1.3 bar.

Feed tank was filled with 3 L of wastewater solution and TMP is adjusted at the correspondent value of pressure with permeate and retentate valves closed; the apparatus is pressurized by nitrogen, so it was not possible to work in a continuous way. After10 minutes permeate valve was open and flux is checked manually. After this, valve remains opened and flux was measured even three minutes for five times. Following the feed tank was empty and 3 L of distilled water were put inside to estimate flux decline. After each experiment, equipment and membrane were washed with alkaline detergents (P3-Ultrasil 25) and rinsed with distilled water until pH returned to the value of about 7. Chemical cleaning was necessary in order to get outlet fluxes similar to those obtained with distilled water; the cleaning procedure is described in Table 2.

Table 2. Cleaning Procedure

Cleaning Solution	**Concentration**	**Backflush**	**PT [bar]**	**Time [min]**	**Permeate Valve**	**Temperature [°C]**
P3-Ultrasil 25	2%	yes	1.3	30+30	close/open	room
Distilled Water	-	yes	1.8	30	open	50
Distilled Water	-	yes	1.8	30	open	50

3. RESULTS AND DISCUSSION

3.1. Flows

Fig. 2 and 3 shows the flux obtained with 210 kDa membrane, SDS above CMC at different pressure value.

It is possible to note in that there is a constant linear trend for both tests. In the first case the maximum value reached with the solution was 300 l/m^2h, with dirty membrane and distilled water, flows are approximately 900 l/m^2h and 300 l/m^2h. In the second case the maximum value reached with the solution was 150 l/m^2h and with dirty membrane and distilled water, flows are approximately 250 l/m^2h and 120 l/m^2h.

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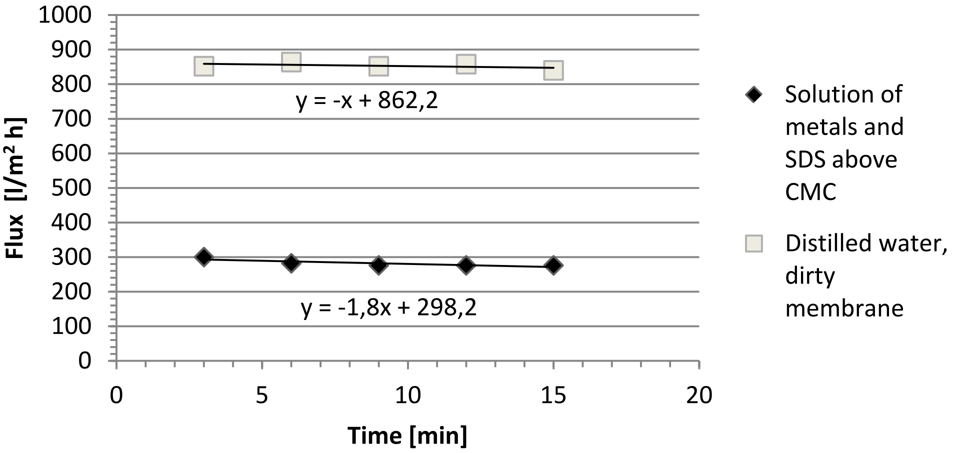


Figure 2. Membrane flows for test number 4 (2.8 bar)

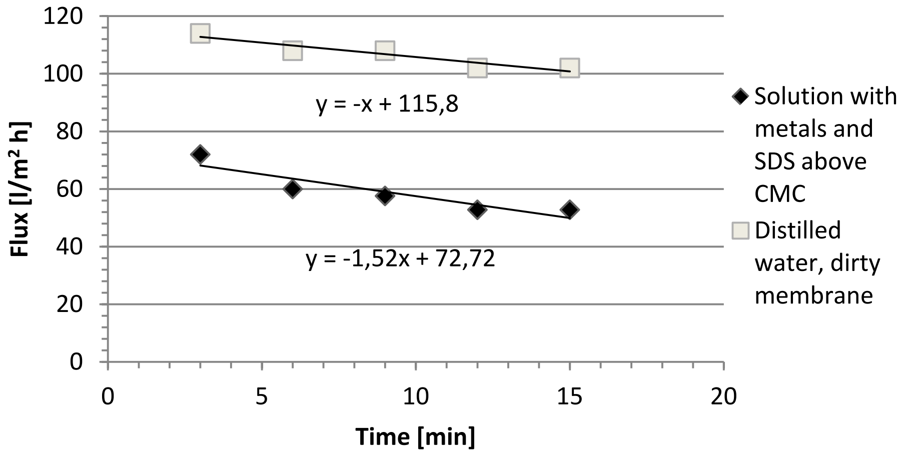


Figure 3. Membrane flows for test number 3 (0.8 bar)

3.2 Rejection Coefficients

Table 3 and the following figures show the results of the experiments in term of rejection coefficients. This coefficient has been calculated as follow:

$$\sigma = \left(1 - \frac{C_p}{C_s}\right) \text{x } 100 \quad (1)$$

where C_p and C_s were permeate and solution concentration, respectively.

Table 3. Rejection coefficients for metal removal

Test	SDS concentration [mg/L]	Pressure [bar]	Mn Rejection [%]	Zn Rejection [%]	Ni Rejection [%]
1	0	0.8	5.78	5.42	5.84
2	0	2.8	0.88	0.86	0.26
3	x2	0.8	97.05	98.09	96.00
4	x2	2.8	54.26	56.33	54.20
5	x1	1.3	80.66	81.60	79.76

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The removal yields were comprised from very low values, near to zero, until values greater than 95%. The best values of the rejection coefficients are obtained in the test 3 with low values of the transmembrane pressure, 210 kDa membrane and SDS above CMC. In these conditions 97%, 98% and 96% of Mn, Zn and Ni were removed, respectively.

The very low yields were obtained in absence of SDS. The surfactant had a strong positive effect for the removal of the all metals, and this trend was reported in the Figure 5 in which the effect of pressure and SDS concentration for the rejection of manganese was showed. The other metals had the same trend of manganese.

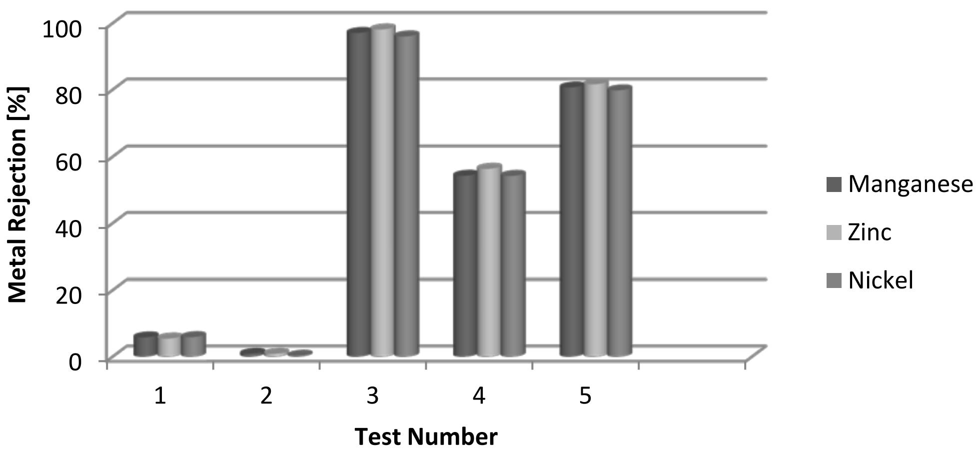


Figure 4: Rejection coefficients for manganese, zinc and nickel removal

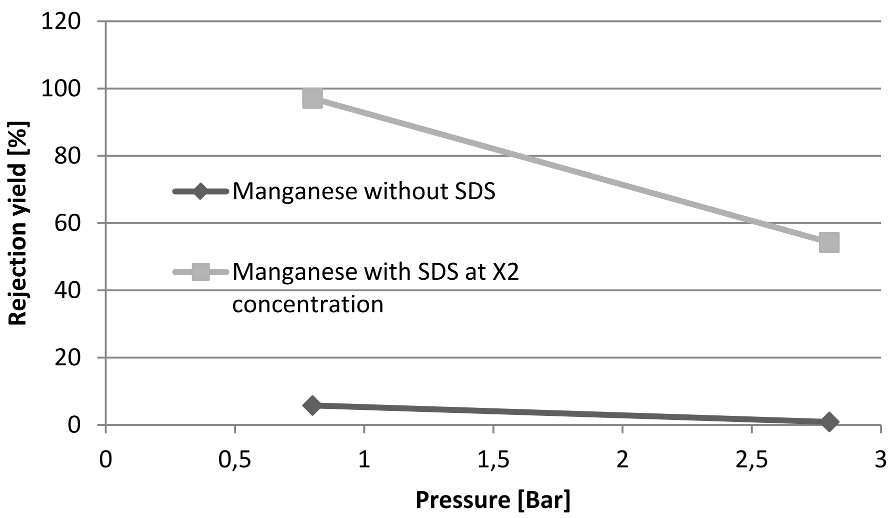


Figure 5: Rejection yields of manganese as a function of SDS concentration

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4. CONCLUSIONS

In this paper the purification of residual leach liquors from hydrometallurgical process of NiMH spent batteries through Micellar Enhanced Ultra Filtration was investigated. The initial solution had a concentration of 9.86 mg/L of Zn,18 mg/L of Mn and 7.33 mg/L of Ni, respectively.

The removal of Ni, Mn and Zn from solutions was studied as a function of surfactant concentration and pressure of filtration using a membrane with size of 210 kDa.

The results of the tests showed that the presence of surfactant was necessary for the rejection of the all metals; in fact this factor had a strong positive effect. Moreover the pressure filtration had a positive effect The maximum removal of the metals was 97% for manganese, 98% for zinc and 80% for nickel. The optimal conditions, among those investigated, were 210 kDa of membrane in the presence of surfactant with a concentration of X_2 and 0.8 bar of pressure filtration for manganese and zinc. Instead for nickel a removal of 80% was obtained using a membrane with 210 kDa, a concentration of surfactant of X_1 with a pressure of 1.3 bar.

It was possible to conclude that zinc, manganese and nickel could be effectively removed from solution that simulated a residual liquors coming from treatment of NiMH spent batteries in the using a membrane with 210 kDa in the presence of surfactant and 0.8 bar of pressure filtration. In these conditions the removal yields were more than 95% for manganese and zinc and more than 65% for nickel.

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References

[1] http://ec.europa.eu/environment/waste/batteries/index.htm#top-page
[2] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:266:0001:0014:en:PDF
[3] http://faolex.fao.org/docs/pdf/eur83700.pdf
[4] http://ec.europa.eu/eurostat/web/waste/key-waste-streams/batteries
[5] http://www.repubblica.it/ambiente/2014/05/13/news/italia_raccolta_pile_esauste-86006506/?refresh_ce
[6] Muller, T., Friedrich, B., 2006.Development of a recycling process for nickel-metal hydride batteries. *J. PowerSources***158**, 1498-1509.
[7] L’industria automotive mondiale nel 2013, Associazione nazionale filiera, Industria Automobistica
[8] http://www.greenstart.it/approfondimento/i-dati-di-vendita-di-auto-elettriche-e-ibride-settembre-2014-italia-1225
[9] Zhang, P.W., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1999. Recovery of metal values from spent nickel-metal hydride rechargeable batteries. *J. PowerSources*, **77**, 116–122.
[10] Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M.R., 2002. Rare earths recovery from NiMH spent batteries. *Hydrometallurgy***66**, 135-139.
[11] Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M., 2005.Characterization and leaching od NiCd and NiMH spent batteries for the recovery of metals. *WasteManagement***25**, 221-226.
[12] Li, L.Y., Xu, S.M., Ju, Z.J., Wu, F., 2009. Recovery of Ni, Co and rare earths from spent Ni-metal hydride batteries and preparation of spherical Ni(OH)2. *Hydrometallurgy*, **100**, 41–46.
[13] Bertoul, D.A., Bernardes, A.M., Tenorio, J.A.S., 2009. Spent NiMH batteries – The role of selective precipitation in the recovery of valuable metals. *Journal of Power Sources***193**, 914-923.
[14] Bertoul, D.A., Amado, F.D.R, Veit, H., Ferreira, J.Z., Bernardes A.M., 2012. Recovery of nickel and cobalt from spent NiMH batteries by electrowinning. *Chemical Engineering Technology***25**, 2084-2092.
[15] Nayl, A.A., 2010. Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336. *Journal of Hazardous Materials***173**, 223-230.
[16] Innocenzi, V., Vegliò, F., 2012a. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. *J. Power Sources***211**, 184-191.
[17] Gasser, M.S., Aly, M.I., 2013. Separation and recovery of rare earth elements from spent nickel-metal-hydride batteries using synthetic adsorbent. International *Journal of Mineral Processing***121**, 31-38.
[18] Zhang, P.W., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1998. Hydrometallurgical process for recovery of metal values from spent nickel metal hydride secondary batteries. *Hydrometallurgy*, **50**, 61–75.

[19] Tzanetakis, N., Scott, K., 2004. Recycling of nickel-metal hydride batteries. I: Dissolution and Solvent extraction of metals. *Journal of Chemical Technology and Biotechnology***79**, 916-926.
[20] Kanamori, T., Matsuda, M., Miyake, M., 2009. Recovery of rare metal coumponds from nickel-metal hydride battery waste and their application to CH4 dry reforming catalyst. *Journal of Hazardous Materials***169**, 240-245.
[21] Fernandes, A., Afonso, J.C., Dutra, A.J.B., 2013. Separation of nickel (II), cobalt (II) and lanthanides from spent NiMH batteries by hydrochloric acid leaching, solvent extraction and precipitation. *Hydrometallurgy***133**, 27-43.
[22] Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. *Journal of Power Sources***195**, 3735-3741.
[23] Innocenzi, V., Vegliò, F., 2012b. Separation of manganese, zinc and nickel from leaching solution of nickel-metal hydride spent batteries by solvent extraction. *Hydrometallurgy***129/130**, 50-58.
[24] Ferella F., M. Prisciandaro, I. De Michelis, F. Vegliò, 2007Removal of heavy metals by surfactant enhanced ultrafiltration from wastewaters, *Desalination***207**, 125-133.
[25] Innocenzi V., F. Tortora, M. Prisciandaro, F. Vegliò, Heavy metal removal from liquid wastes by using Micellar Enhanced Ultra Filtration, *Euromed Congress 2015*, Palermo, May 2015.
[26] Tortora F., V. Innocenzi, M. Prisciandaro, F. Vegliò, Removal of Nickel and Cobalt from Liquid wastes aimed at surfactant and metal recovery, Desalination and Water Treatment (2016), pp. 1-7 published on line DOI: 10.1080/19443994.2016.1180475.

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Numerical algorithm compared with analytic solution to solve an inverse problem of contamination source in a river

G. F. Santonastaso, A. Di Nardo*, M. Di Natale, M. Iervolino, D. Musmarra

Department of Civil Engineering, Design, Building and Environmental,
Second University of Naples, Aversa, 81031, Italy.
*Corresponding author: Email: armando.dinardo@unina2.it

Abstract

The identification of the source of a contamination in a river, either accidental or intentional, is of extreme interest for the technical and scientific communities, because it is the preliminary step towards risk mitigation for human, animal and vegetable health. Recently, the development of innovative wireless sensors, coupled with computational tools appropriate to analyse big data almost in real-time, offers novel opportunities to develop early-warning systems for the protection of surface waters. Within this framework, it is possible to use exact solutions of the equations describing the conservation of contaminant mass to identify the location where contamination took place, if the geometry, the hydraulic parameters and the boundary conditions are sufficiently simple. On the other hand, for more general conditions these equations can be solved only numerically. In both cases, an inverse problem can be formulated coupling the appropriate solution method to heuristic optimization algorithms that provide an optimal solution for the magnitude, the shape and the position of the contamination sources. In this paper, a novel identification algorithm, based on a parametric method for the contamination inputs, a genetic algorithm for optimization problem and a statistical approach to define the best solution, is proposed. As far as the mass conservation equation is concerned, the response to a rectangular contamination pattern is computed by both the exact solution based on the convolution of the pulse response and the finite difference Cranck-Nicolson discretization of the governing equations. These procedures have been applied on a hypothetical case study of Volturno river in South of Italy, close to the town of Caserta, modelled as one-dimensional flow. The comparison between the two approaches, exact and numerical, to the governing equation solution provides interesting results in terms of effectiveness, time responses and model limitations, useful to implement an identification network of smart sensors

Keywords: smart water network; surface water; biosensors; contamination; water protection

1. INTRODUCTION

The serious problem of river water contamination is even more frequent and essentially due to industrialization, rapid population growth and increase in urbanization [1], but also to the use of chemical agents in agricultural [2]. These contamination events can occur also accidentally, for example, during the interruption of service of a treatment plant but, unfortunately, in some cases, are intentionally caused through non-authorized discharges of urban wastewaters.

To minimize the contamination risks of surface water, some actions have been adopted to control the anthropic activities both in industries as in agricultural. Recently, the 2008/105/EC Directive established a list of 33 priority substances requiring special attention concerning water protection, of which one-third are pesticides [3]. Anyway, the current techniques used for the determination of pollutant concentration, based on sophisticated laboratory equipment, are inherently off-line, thereby being unable to provide the desirable quick response. This approach allows only monitoring

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occasionally the water quality but not to identify the contamination sources that requires many distributed spatially and temporally measures. Indeed, the second aim can be obtained only using a large sensor network and a real-time monitoring that can allow to build a Early Warning System able to recognize the contamination source and rapidly to alert the police and public authorities. Nevertheless, these requirements can be very expensive. In other terms, a dense grid of low-cost sensors gives more protection than just a few complex stations.

The recent development of biosensors [4, 5], based on different technologies, as on Luminescent bacteria, combined with the quantitative measurement of chemical parameters applying standard spectrophotometric/fluorimetric methods, Quartz Crystal Microbalances (QCMs), Fluorimetric methods using specific organic liquid reagents, Nanofiber materials with electrochemical techniques, Optofluidic jet waveguide, Microwave resonator, Electrochemical, Bio-based electrodes, etc. [5] seems highly promising and able to provide devices for real-time monitoring of critical situations also with low costs [2]. These technologies can be arranged in a sensor network for water early-warning in which the sensors are the eyes of the system.

The threat of accidental contamination of water systems is not new, but in the past few years considerable effort has been devoted to develop mathematical algorithms in support of contamination events in water distribution networks [6]. The detection of the pollution source as the solution of an inverse problem involving contaminant transport in a river is less investigated. Basic concepts can be found in the works by [7] and [8], whereas the interested reader is referred to the paper by [9] for a detailed statement of the problem. Apart from the inherent difficulties resulting from the ill-posedness of this nonlinear inverse problem [10], most of the practical approaches to this problem require the repeated solution of the governing equations describing contaminant transport. From the computational point of view, this requirement may become extremely demanding if discrete methods like Finite Differences or Finite Volumes are used. Moreover, the above methods may suffer from the consequences of finite accuracy, like diffusive or dispersive errors [11]. To overcome these difficulties, the present paper explores the use of exact solution of the contaminant transport equation built by means of the convolution integral of the impulse response, accounting for convective and diffusive transport, comparing the results of the pollution source detection for a sample application. A heuristic optimization algorithm implemented in MATLAB, is used. Specifically, a smart monitoring system of a river reach by an innovative biosensors network, able to identify contamination source, is considered, with the aim to detect the position, magnitude, lifespan and time of the local contamination to allow the localization of source in a reach enclosed between by two biosensors.

2. MATERIALS AND METHODS

The methodology proposed is based on the comparison between the analytical solution and a numerical algorithm in order to identify the most likely position X, magnitude C^*, lifespan δ and injection time T of the impulsive contamination in a river reach equipped with two innovative biosensors, upstream and downstream, as reported in the Figure 1. As already proposed in [2], the sensor network can be realised by placing an array of B_n smart biosensors along the river, illustrated schematically with an indefinite line in the Figure 1. In particular, the river can be split into several reaches, generally bounded by two biosensors B_s and B_{s+1}. Given the number of biosensors, it is possible to limit the space where the contamination may have occurred in terms of some identification variables: position X, magnitude C^*, lifespan δ and injection time T. However, the issue concerning monitoring of rivers in detail is beyond the scope of the paper.

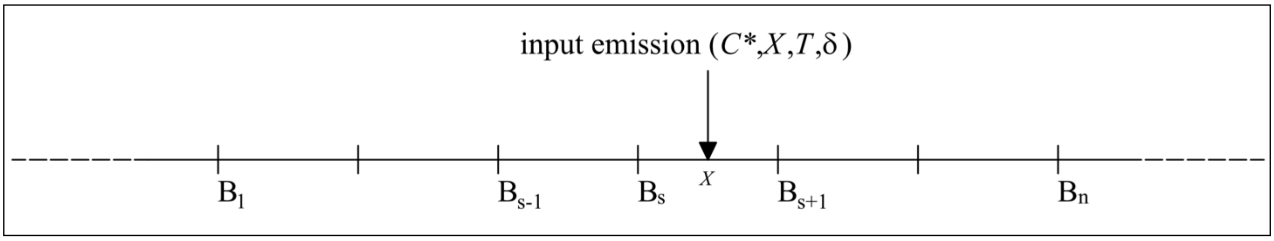


Figure 1. Identification variables and network sector.

The identification process is achieved comparing measures in B_s and B_{s+1} versus simulated values using a least squares formulations applied to early warning systems, minimizing the difference between measured and simulated concentration predictions, in an attempt to locate the position X, magnitude C^*, lifespan δ and time T. As known, the transport of a conservative pollutant dissolved in the flowing water can be described as an advection-dispersion process and the 1-D model equation for a non-prismatic open channel can be written as follows [12]:

$$\frac{\partial}{\partial t}(A \cdot C) = -\frac{\partial}{\partial x}(Q \cdot C) + \frac{\partial}{\partial x}\left(A \cdot D \frac{\partial C}{\partial x}\right) \tag{1}$$

where A is the river cross-section area, C the average solute concentration, D the dispersion coefficient, Q is the volumetric flow rate, t is the time and x is the streamwise coordinate. For steady uniform flow, when A=const, Q=const and D=const., Equation (1) simplifies into:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \tag{2}$$

Furthermore, to take into account the injection of the pollutant in the channel, it can be assumed that the mixing with ambient fluid is complete and instantaneous. Thus the downstream concentration can be computed as follows:

$$C_x = \frac{C_{x-1} \cdot Q + C_{\text{pollutant}} \cdot Q_{\text{pollutant}}}{Q + Q_{\text{pollutant}}} \tag{3}$$

Where the C_x is the pollutant concentration just downstream the injection, C_{x-1} is the upstream pollutant concentration, $Q_{pollutant}$ and $C_{pollutant}$ are the flow rate and the concentration of pollutant, respectively.

2.1 Analytical or numerical solution for identification of contaminant

As far as the two contamination scenarios CS1 and CS2 are concerned, the partial differential equation PDE (2) may be solved exactly. The following boundary conditions applies to both scenarios:

$$\begin{cases} C = \text{const} & x = 0 \\ \dfrac{\partial C}{\partial x} = 0 & x = L \end{cases} \tag{4}$$

The solution can be straightforwardly constructed with the procedure outlined in [13]. The expression for the concentration can be written as the convolution of the input signal and the concentration for the Dirac function,

$$C(x,t)=\int_0^t Ug(t-\tau)\left[\frac{1}{\sqrt{\pi D\tau}}e^{-\frac{(x-U\tau)^2}{4D\tau}}-\frac{U}{2D}e^{\frac{Ux}{D}}\mathrm{erfc}\left(\frac{x+U\tau}{\sqrt{\pi D\tau}}\right)\right]\mathrm{d}\tau \tag{5}$$

where the arbitrary input function, $g(t)$ results from the combination of eq. (3) with the scenario-specific pollutograph. Alternatively, the partial differential equation PDE (2) with the same boundary conditions described above may be also solved numerically with the Crank & Nicolson finite-difference method [14, 15].

2.2 Identification process for pollution source detection

The identification process is based on a real-time process driven by analysis of the measures of a couple of biosensors in the network, B_s and B_{s+1} . The identification of position X, magnitude C^*, lifespan δ and time delay T of the contamination is carried out by an optimization algorithm.

Specifically, neglecting spills as phase transformation during the flow, the total mass of contaminant injected in the reach is conserved and it is measured by the downstream biosensors B_{s+1}. Based on this information, it is possible to define the parameter C^* for a rectangular injection, discharging upstream at distance $-X$ with the same total mass measured by the downstream sensor B_{s+1} with a lifespan δ and a time delay T:

$$C^* = \frac{1}{\delta}\int_0^{\delta_m} C_m \cdot dt \tag{6}$$

where δ_m and C_m are the measured lifespan and concentration of pollutant in B_{s+1}. The identification process is carried out minimizing the following objective function (FO):

$$FO = \sum_{t=0}^{t_{max}} \sqrt{\left(C_m(t) - C_i(t)\right)^2} \tag{7}$$

where t_{max} is the total time of simulation, $C_i(t)$ is the pollutant concentration at time t computed in the downstream section by numerical solution of equation (2), and $C_m(t)$ is the measured concentration at time t. For the minimization of FO (6) a Genetic Algorithm (GA) [16] was used. The identification process is schematically illustrated in the flow chart of Figure 2.

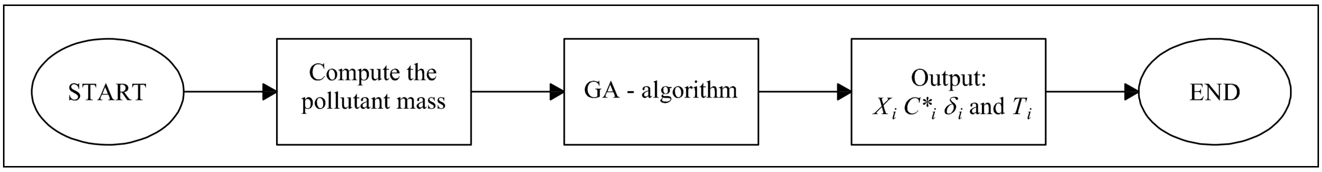


Figure 2. Flow chart of pollution source identification algorithm

2.3 Input contamination scenarios

The contaminant emission scenarios, used as inputs in the comparison, are assumed as a rectangular pollutograph (Figure 3), whose parameters are the peak concentration magnitude C^*, lifespan δ and time delay T. Moreover, two Contamination Scenarios (CS) have been investigated: CS1) a rectangular pollutograph in a clean reach (i.e. null concentration upstream); CS2) a rectangular pollutograph over a constant upstream concentration C_{in} (measured by biosensor B_s).

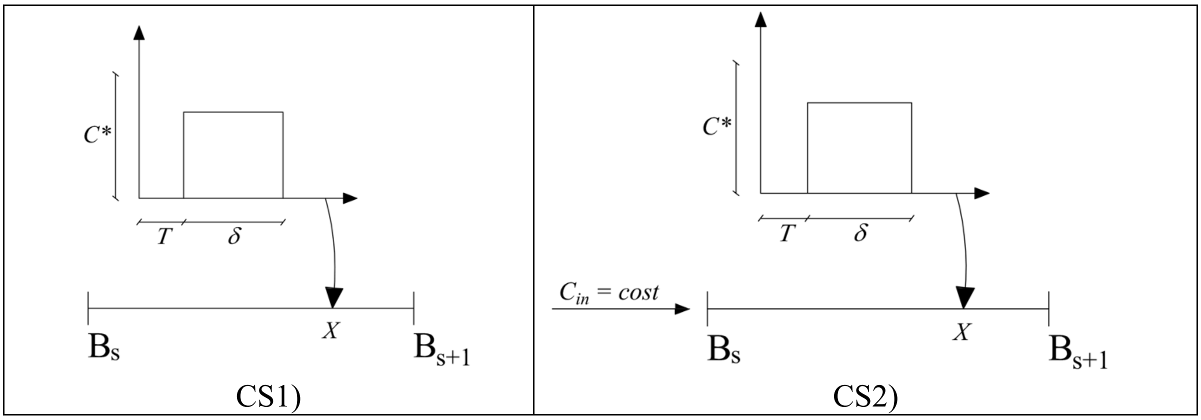


Figure 3. Two Input Emission scenarios CS1 and CS2.

3. RESULTS AND DISCUSSION

The comparison between two approach, analytical and numerical, has been tested on a synthetic example, already proposed in [2] in which the considered river strech cosidenred has a length of 10 km, a flow rate Q=20 m^3/sec, mean velocity U=0.7 m/sec and dispersion coefficient D=10 m^2/sec in compliance with hydraulic properties of a typical Italian alluvial river.

The analysis is conducted starting from the parameters of theoretical inputs of contamination (C_{in}, $C_{pollutant}$, δ, X, T) which are used to generate the synthetic "measured concentration" (MC) in the two scenarios. Their values are reported in Table 1. For sake of simplicity, in the following analysis, the delay T has been set equal to zero. Furthermore, the contaminant volume injected in both scenariohas been assumed equal to W=10 m^3. Figure 4 illustrates with continuous line the time evolution of the MC for Contamination Scenario 1 (CS1) and (CS2).

Table 1. Contamination parameters

	CS1	**CS2**
C_{in} [mg/l]	0.00	0.30
$C_{pollutant}$ [mg/l]	$5 \cdot 10^3$	$5 \cdot 10^3$
C^* [mg/l]	2.626	3.218
δ [sec]	900	900
X [m]	3500	6000
T [sec]	0	0
W [m^3]	10	10

In Table 2, the identification results are reported, showing the effectiveness of the proposed approach based on the convolution integral (5): in both scenarios, very low values of FO, along with practically the correct value of the injection point (with a maximum error of 50 m) of the concentration magnitude C^*, the positioning X, lifespan δ and time delay T, have been identified.

As far as the numerical solution of Eq. (2) is concerned, the analysis has been repeated for three values of the space step Δx, assuming at first the typical value Δx=28 m, a larger ($2\Delta x$) and a smaller one ($\Delta x/2$). The computational time needed to solve the identification problem is also reported in Table 2.

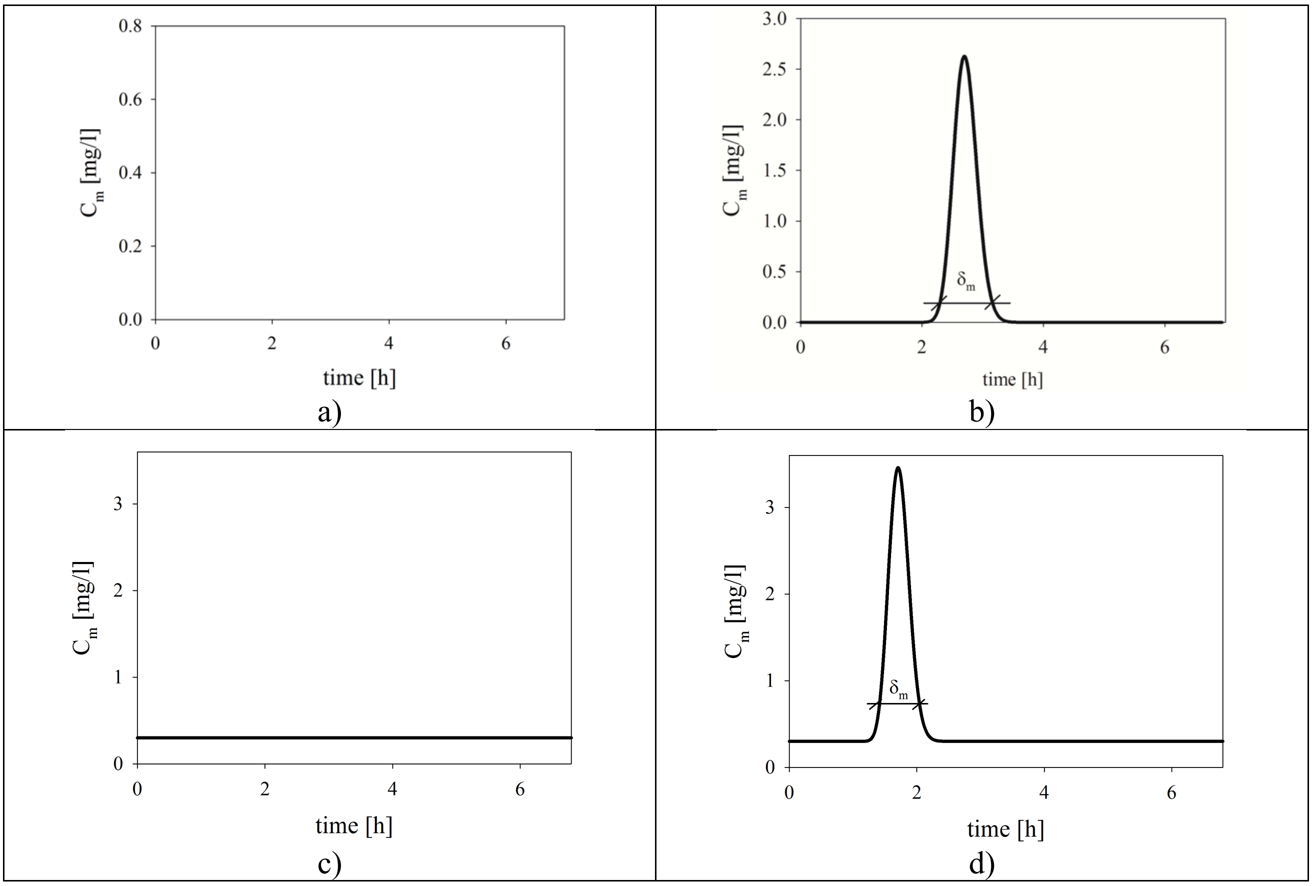


Figure 4. Measured Concentration in B_s and B_{s+1} respectively for CS1 (a)-(b) and CS2 (c)-(d).

Table 2. Identification results for SC1 and SC2

		Magnitude C^* [mg/l]	**Lifespan δ [sec]**	**Positioning X [m]**	**Execution Time [sec]**	**FO**
Scenario 1	Analytical	2.627	900	3500	$3\cdot10^2$	$7.13\cdot10^{-12}$
	Numerical	2.665	910	3503	$6\cdot10^3$	190.48
	Numerical [Δ*x*/2]	2.667	920	3498	$1\cdot10^5$	229.10
	Numerical [2Δ*x*]	2.652	820	3495	$2\cdot10^3$	638.92
Scenario 2	Analytical	3.449	914	6004	$2\cdot10^3$	99.26
	Numerical	3.544	909	5986	$3\cdot10^3$	76.98
	Numerical [Δ*x*/2]	3.532	933	5987	$4\cdot10^4$	293.36
	Numerical [2Δ*x*]	3.547	748	5983	$2\cdot10^3$	707.92

In order to provide a more detailed assessment of the performance of the two approaches, Table 3 and Table 4 reports the values of four statistics of the temporal distribution of the Measured Concentration at the downstream sensor, namely the mean concentration, the Standard Deviation (S.D.), the Skewness and the Curtosis.

Table 2 and 3 show that the values of the parameters identified through the numerical solution of the governing equations are in worse agreement with the true ones compared with those obtained with the aid of the exact analytical solution. Correspondingly, the FO values are generally larger than those corresponding to the analytical solution.

Table 3. Identification results for SC1

		Mean	S.d.	Skewness	Curtosis
Scenario 1	Analytical	0.1802	0.3027	3.3014	9.9050
	Numerical	0.1790	0.3059	3.3448	10.2090
	Numerical [$\Delta x/2$]	0.1789	0.3053	3.3330	10.1166
	Numerical [$2\Delta x$]	0.1790	0.3061	3.3468	10.2250

Table 4. Identification results for SC2

		Mean	S.d.	Skewness	Curtosis
Scenario 2	Analytical	0.4802	0.3703	3.6907	12.7691
	Numerical	0.4794	0.3813	3.7658	13.3606
	Numerical [$\Delta x/2$]	0.4794	0.3798	3.7575	13.2949
	Numerical [$2\Delta x$]	0.4778	0.3797	3.7845	13.5033

Moreover, a slight but appreciable dependence of the identification results on the mesh spacing adopted is found. Finally, as far as the computational cost is concerned, the execution time is comparable only for the coarser mesh. The finest resolution considered caused an increase of more than one order of magnitude of the execution time, without any significant increase in the accuracy of pollutograph parameter estimation.

As far as the time statistics are concerned, the analytical ones are found to coincide with the true ones, whereas those based on numerical solution are affected by a mesh-dependent inaccuracy, which in the present example is about 5 % for the higher-order statistics.
Based on the above results, in both the scenarios the exact solution therefore allows more accurate and efficient solution to the pollution source identification problem. However, this advantage is counterbalanced by the restriction to simple geometries and constant parameters, which limit the validity the exact solution (5). On the other hand, the procedure based on the numerical solution of the transport equation can be straightforwardly extended to the case of non-uniform distribution of the flow velocity and/or of the diffusion coefficient, to one-dimensional time-dependent flows as well as to contamination problem involving even two- or three-dimensional flow fields, provided that a suitable computational power is available.
Further research will be devoted to investigate the effect on the identification of potential source of disturbance such as measuring errors, uncertainties in the flow parameters, unknown shape of the pollutograph.

4. CONCLUSIONS

The identification of the pollution source in a river may be regarded as an inverse problem driven by the measured concentrations upstream and downstream the injection point. Common approaches to this problem require the repeated solution of the governing equations expressing the convective /diffusive contaminant transport, which is usually performed by means of discrete numerical methods. In the present paper, an alternative strategy based on the use of exact solution of the contaminant transport equation built by means of the convolution integral of the impulse response, has been explored. These two approaches have been embedded in an heuristic optimization algorithm and compared with reference to a sample synthetic application. In the considered examples, the approach based on the exact solution provided at the same time more accurate results and a considerable reduction of the computational cost. However, the procedure based on the numerical solution of the transport equation can be extended more easily to more complex flow fields of certain practical applications, for which the exact solution is not available.

References

1. Burchard-Levine, A., Liu, S., Vince, F., Li, M., Ostfeld, A. 2014. A hybrid evolutionary data driven model for river water quality early warning, *Journal of Environmental Management*, **143**, 8 – 16.
2. Di Nardo, A., Santonastaso, G.F., Battaglia, R., Musmarra, D., Tuccinardi, F.P., Castaldo, F., Della Ventura, B., Iervolino, M., Velotta, R. 2015a. Smart identification system of surface water contamination by an innovative biosensor network, *Proceedings of Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE) and to the SECOTOX Conference*, Myconos, 14 June – 18 June 2015.
3. European Communities, 2008. Directive 2008/105/EC of the European Parliament and of the Council.
4. Funari, R., Della Ventura, B., Carrieri, R., Morra, L., Lahoz, E., Gesuele, F., Altucci, C., Velotta, R., 2015. Detection of Parathion and Patulin by Quartz-Crystal Microbalance Functionalized by the Photonics Immobilization Technique. *Biosensors and Bioelectronics* , **67**, 224 – 229.
5. Di Nardo, A., Alcocer-Yamanaka, V.H., Altucci, C., Battaglia, R., Bernini, R., Bodini, S., Bortone, I., Bourguett-Ortiz, V.J., Cammissa, A., Capasso, S., Cascetta, F., Cocco, M., D'Acunto, M., Della Ventura, B., De Martino, F., Di Mauro, A., Di Natale, M., Doveri, M., El Mansouri, B., Funari, R., Gesuele, F., Greco, R., Iovino, P., Koenig, R., Korakis, T., Laspidou, C.S., Lupi, L., Maietta, M., Musmarra, D., Paleari, O., Santonastaso, G.F., Savic, D., Scozzari, A., Soldovieri, F., Smorra, F., Tuccinardi, F.P., Tzatchkov, V.G., Vamvakeridou-Lyroudia, L.S., Velotta, R., Venticinque, S., Vetrano, B. 2015b. New Perspectives for Smart Water Network monitoring, partitioning and protection with innovative On-line Measuring Sensors**,** *Proceedings of IAHR 2015 Conference*, Delft, 28 June-2 July 2015.
6. Kessler, A., Ostfeld, A., and Sinai, G. 1998. Detecting Accidental Contaminations in Municipal Water Networks. *Journal of Water Resources Planning and Management*, **124(4),** 192–198.
7. Kirsch, A. 1996. *An Introduction to the Mathematical Theory of Inverse Problems*, Applied Mathematical Sciences, Berlin, Springer.
8. Okubo, 1980. *Diffusion and Ecological Problems: Mathematical Models*, New York, Springer.
9. El Badia, A., Ha-Duong, T., Hamdi, A. 2005. Identification of a point source in a linear advection–dispersion–reaction equation: application to a pollution source problem. *Inverse Problems*, **21(3),** 1–17.
10. Belgacem, F. B. 2012. Identifiability for the pointwise source detection in Fisher's reaction–diffusion equation. *Inverse problems*, **28(6),** 065015.
11. Hirsch, C. 2007. *Numerical Computation of Internal and External Flows: The Fundamentals of Computational Fluid Dynamics: The Fundamentals of Computational Fluid Dynamics*. Butterworth-Heinemann.
12. Fischer, H. B., List, E. J., Koh, R. C. Y., Imberoer, J., Brooks., N. H., 1979. *Mixing in Inland and Coastal Waters*. Academic Press, California.
13. Van Genuchten, M.T., Leij, F.J., Skaggs, T.H., Toride, N., Bradford, S.A., Pontedeiro, E.M. 2013. Exact analytical solutions for contaminant transport in rivers. 1. The equilibrium advection-dispersion equation. *Journal of Hydrology and Hydromechanics*, **61(2)**, 146–160.
14. Crank, J., Nicolson, P., 1947. A practical method for numerical evaluation of solutions of partial differential equations of the heat conduction type. *Mathematical Proceedings of the Cambridge Philosophical Society*, **43(1)**, 50 – 67.
15. Fletcher, C. A. J., 1983. A comparison of finite element and finite difference of the one-and two-dimensional Burgers' equations. *Journal of Computational Physics*, **51(1)**, 159 – 188.
16. Goldberg, D. E., 1989. *Genetic Algorithms in Search, Optimization and Machine Learning.* Addison-Wesley Longman Publishing Co., Inc. Boston, MA, USA ©1989.

Experimental study on single and competitive adsorption of benzene and toluene from model groundwater

A. Erto[1*], S. Chianese[2], A. Lancia[1], D. Musmarra[2]

[1] Università degli Studi di Napoli Federico II, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio 80, 80125, Napoli, Italy.
[2] Seconda Università degli Studi di Napoli, Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Via Roma 29, 81031, Aversa (CE), Italy.
* Corresponding author: Email: aleserto@unina.it

Abstract

An experimental and modelling analysis of benzene/toluene removal from model groundwater by adsorption on a commercial activated carbon was carried out in single-compound and binary systems. Single-compound results show that toluene is adsorbed more than benzene and an increase in its adsorption capacity gives rise to lateral interactions between adsorbed molecules. This is probably due to the presence of electron-donor methyl groups, which determine an increase in the electronegativity of the aromatic ring and, consequently, stronger attractions to the nucleophilic carbon basal plane. Binary results indicate that toluene has the highest adsorption capacity, but some competitive effects arise for both analytes. A modelling analysis of the binary system shows that the Ideal Adsorbed Solution Theory (IAST) model can provide a very good prediction of adsorption data for both compounds in all the investigated range of concentrations.

Keywords: groundwater; benzene; toluene; competitive adsorption; isosteric heat of adsorption

1. INTRODUCTION

Organic micropollutants, such as benzene and toluene, are typical groundwater contaminants and their occurrence is mainly due to accidental leakages and illegal discharges of gasoline or petrol derivatives [1,2]. These compounds are toxic; in particular, benzene is formally recognized as carcinogenic [3]. Accordingly, maximum contaminant levels for groundwater are established worldwide.

The removal of these compounds from polluted groundwater is a necessary task and adsorption is widely used as a remediation technique. Adsorption can be applied as an *ex-situ* treatment, like in the Pump & Treat technique, or as an *in-situ* treatment, like in permeable barriers made of adsorbing materials (Permeable Adsorptive Barriers) [4,5]. Regardless of the specific application, adsorption has proven to be a reliable technology, characterized by good efficiency and great versatility that make it suitable to be applied also when a multiple contamination occurs [6,7]. In the last years, several experimental works have been carried out to assess the effectiveness of various sorbents, both commercial [8,9] and low-cost materials [10,11], in capturing benzene and its derivatives, and activated carbon (AC) seems to be the most frequently used material.

In the latest scientific guidelines, adsorption is listed among the BATs (best available techniques) for groundwater depuration [12] and there is a renewed interest in a critical study of adsorption phenomena, focusing on each single sorbate and its peculiar adsorption properties.

As to aromatic compounds in their molecular form (i.e. when solution pH<<pKa), it is commonly believed that a high concentration of acidic oxygen-containing surface groups is very detrimental to adsorption due to a preferential water adsorption, regardless of sorbate polarity

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[13,14]. On the contrary, a high micropore volume enhances the adsorption of aromatic compounds, even if stearic hindrance phenomena might occur [15]. However, the influence of the molecule structure and, in particular, of the substituent functional groups on aromatic rings should be taken into account in order to assess the adsorption dynamics of specific aromatic compounds. Hence, this work aims at analysing the mechanism of adsorption of benzene and toluene in model groundwater on a commercial granular activated carbon (GAC) and their influence on competitive adsorption. Experimental tests were carried out both in single and binary systems, by varying some of the main thermodynamic parameters (i.e. concentration and temperature). A thermodynamic analysis was carried out in order to assess the energetic interactions between sorbates and GAC surface, so to address the differences in their adsorption capacity. Finally, a modelling analysis was made.

2. MATERIALS AND METHODS

The activated carbon used in this research work (Filtrasorb 400, F400, from Calgon Carbon Corporation) is mainly microporous (micropore volume equal to 0.33 $cm^3\ g^{-1}$) and with a BET surface area approximately equal to 900 $m^2\ g^{-1}$. The surface is slightly basic with a pH_{PZC}=8. A complete list of chemical and physical properties is reported in Balsamo et al. [16].

Adsorption tests were carried out in batch mode using an organic-free mineral water whose chemical properties are representative of groundwater (pH = 8 and salinity = 0,46 mM); a complete list of its chemical and physical properties is reported in Erto et al. [17]. The working solutions were prepared by spiking water samples with benzene/toluene stock solution (Sigma Aldrich, 99.0%). A variable amount of activated carbon (0.3-1.5 g) was added to a 100 mL headspace-free glass vessel of mineral water. For single-compound tests, the temperature was varied in the range 10-50°C, while a binary test was made at 20°C. In particular, the binary test was made on samples with the same volume, activated carbon dosage and initial analyte concentration ratio (C^0_{ben}:C^0_{tol} = 1:1, on molar basis) but different benzene and toluene initial concentrations.

Benzene/toluene concentrations were measured with a gas chromatograph (Agilent, GC 6980) equipped with a flame ionization detector (FID). A Purge and Trap system (Tekmar LSC-2000) was adopted for sample extraction.

3. RESULTS AND DISCUSSION

Adsorption tests on single-compound systems were carried out at four different temperatures, in order to determine the trend of isosteric heat of adsorption (ΔH) as a function of surface loading.

Figure 1 reports the adsorption isotherms of benzene and toluene on F400 activated carbon.

The experimental results show that the adsorption capacity of both compounds decreases by increasing temperature, as one would expect given the exothermicity of adsorption phenomena. For each temperature level, toluene is adsorbed more than benzene.

Based on the experimental data of single compounds at different temperatures, the heat of adsorption at constant amounts of adsorbate adsorbed – i.e. the isosteric heat of adsorption (ΔH, $Jmol^{-1}$) - was calculated. This parameter can provide useful indications on the interactions between adsorbate and adsorbent, which, in turn, can be related to the different molecular structure of the adsorbates. The isosteric heat of adsorption corresponds to the ratio of the infinitesimal change in the adsorbate enthalpy and the infinitesimal change in the amount adsorbed. It can be calculated by the known Van't Hoff equation [15,16]:

$$\frac{d\ln(C)}{dT} = -\frac{\Delta H}{RT^2} \quad \text{or} \quad \frac{d\ln(C)}{d(1/T)} = \frac{\Delta H}{R} \tag{1}$$

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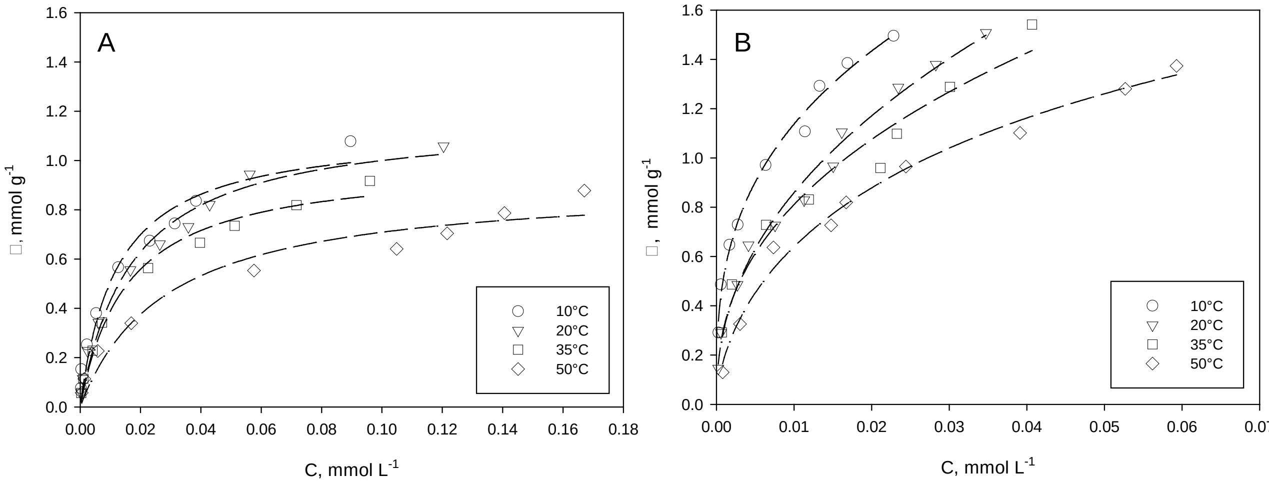


Figure 1. Adsorption isotherms of benzene (A) and toluene (B) onto F400 as a function of temperature. Equilibrium pH=8. Comparison with isotherm models (lines)

To this aim, the benzene/toluene equilibrium concentrations (C) at constant amount of adsorbed compound (ω) are taken from the experimental adsorption isotherm data at different temperatures (from Figures 1A and 1B). The isosteric heat of adsorption (ΔH) at different amounts of adsorbed benzene/toluene can be calculated as the slope of the plot of ln(C) versus (1/T) (Eq.1). The *ΔH* values are shown in Figure 2:

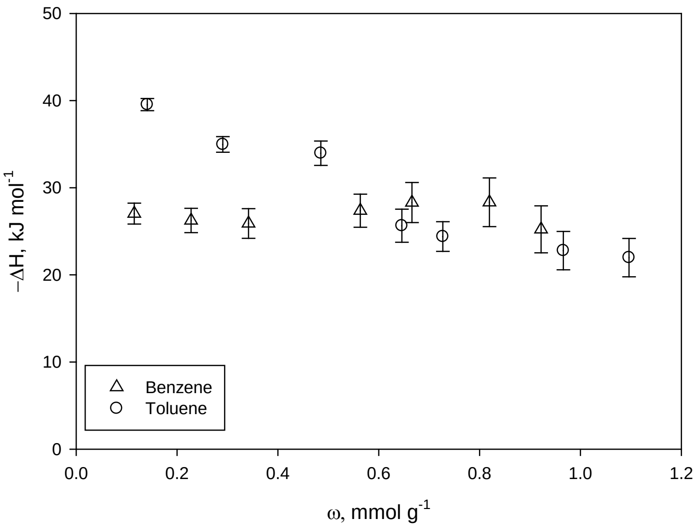


Figure 2. Isosteric heat of adsorption (ΔH) as a function of surface loadings (ω) for benzene and toluene adsorption on GAC.

The thermodynamic analysis shows that, in the range of surface coverage investigated, the isosteric heat of adsorption of benzene is almost constant, also taking into account the error propagation of the analytical determination of benzene equilibrium concentration. This result implies both the energetic homogeneity of adsorption sites towards benzene molecules and the absence of lateral interactions between benzene molecules adsorbed on carbon surface [18]. This is likely due to the benzene molecule structure, perfectly symmetric and non-polar. On the contrary, the toluene isosteric heat of adsorption decreases by increasing surface loading and is always greater than the correspondent value of benzene, in particular for low AC surface coverage. In this case, the result is likely to be ascribed to the interaction between toluene molecules adsorbed rather than to the heteroenergetic character of the adsorption sites [18]. In fact, benzene and toluene adsorption

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mechanisms are expected to be the same; hence, also the active sites involved on the carbon surface are expected to be the same. The only difference lies in the adsorbate molecule structures; indeed, the addition of a methyl group to the aromatic ring of the toluene molecule gives rise to a non-symmetric charge distribution, which can influence the interactions between the adsorbed molecules. In general, it can be stated that the adsorption mechanism of aromatic molecules, such as benzene and toluene, involves dispersion interactions (i.e. London-Van Der Walls forces) between delocalized π-electrons of the condensed polyaromatic carbon sheets and the aromatic ring. The presence of an electron-donor functional group linked to the aromatic ring of toluene (i.e. methyl) determines an increase in the electronegativity of the ring and, consequently, stronger attractions to the nucleophilic carbon basal plane [8,19]. This can also explain the higher adsorption capacity of toluene for each investigated temperature. It can be concluded that the different molecule configuration and polarity are likely to determine the different energetic interactions with the carbon surface, thus influencing also their overall adsorption capacities.

The determination of the best descriptive model for benzene/toluene adsorption onto AC is directly related to the individuation of the adsorption mechanism. Organic compound adsorption is believed to be based on a micropore filling mechanism [18,20] but in dilute systems like those under analysis, adsorption can also be adequately described by different mechanisms [17].

In order to test the classic adsorption model, a nonlinear least-squares regression analysis on benzene and toluene adsorption experimental data was performed. The least residual sum-of-squares (ResSS) was used as a criterion to determine the best fitting parameter of each model.
The isotherm model equations and the model parameters for benzene and toluene adsorption at T=20°C, taken as an example, are reported in Table 1 and 2, respectively. The analysis included the mean value and standard error of the parameters as well as the coefficient of determination (R^2).

Table 1. Isotherm model parameters from benzene adsorption regression analysis at T=20°C

Isotherm	***Equation***	***Parameter***	***Value***			$\mathbf{R^2}$
			Mean	***Std error***	***T-test***	
Temkin	$\omega = B \cdot \ln(KC)$	K (m^3/mol) B (mol/kg)	$1.89\cdot10^3$ 23.46	$4.86\cdot10^2$ 2.299	3.89 13.69	0.959
Freundlich:	$\omega = k \cdot C^n$	K (mol/kg)/(mol/m^3)^n n	2.62 0.680	$2.65\cdot10^{-1}$ $3.87\cdot10^{-1}$	9.87 12.25	0.973
Langmuir:	$\omega = \frac{\omega_{max} K \cdot C}{1 + K \cdot C}$	ω_{max} (mol/kg) ΔG (kJ/mol) K (m^3/mol)	1.17 -9.88 $5.77\cdot10^1$	$7.05\cdot10^{-2}$ $3.2\cdot10^{-1}$ $1.09\cdot10^1$	16.65 22.82 5.31	0.994
Langmuir-Freundlich:	$\omega = \frac{\omega_{max}(K \cdot C)^n}{1 + (K \cdot C)^n}$	ω_{max} (mol/kg) K (m^3/mol) n	1.60 8.54 $6.73\cdot10^{-1}$	$2.12\cdot10^{-1}$ 4.14 $6.79\cdot10^{-2}$	7.55 2.06 9.90	0.979
Dubinin-Radushkevich:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E}\ln\left(\frac{c_s}{c}\right)\right)^2\right]$	ω_{max} (mol/kg) E (kJ/mol)	2.41 $1.45\cdot10^1$	0.71 2.14	3.41 6.77	0.990
Dubinin-Astakhov:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E}\ln\left(\frac{c_s}{c}\right)\right)^n\right]$	ω_{max} (mol/kg) E (kJ/mol) n	1.75 $1.68\cdot10^1$ 2.65	$2.63\cdot10^{-1}$ 1.05 0.39	6.66 16.03 6.73	0.994

The benzene adsorption data analysis shows that the best fitting models are Langmuir and Dubinin-Astakov. However, the fundamental hypotheses of these models are markedly different, i.e. monolayer adsorption on isoenergetic sites and multilayer pore filling mechanism on

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heteroenergetic sites, respectively. Based on the isosteric heat of adsorption analysis, it was concluded that benzene adsorption on AC is isoenergetic in the experimental conditions investigated. Hence, even if multilayer adsorption cannot be definitely dismissed dealing with an organic compound, in dilute solutions benzene adsorption is likely to occur following the monolayer mechanism adequately described by the Langmuir model (Figure 1A).
For toluene adsorption data, the best fitting models are Freundlich, Langmuir-Freundlich and Dubinin-Astakov, while the Langmuir model is far less effective. Also in this case, the results are consistent with the outcomes of the isosteric heat of adsorption analysis, which highlighted the presence of heteroenergetic interactions between toluene molecules and AC surface, which are incompatible with the Langmuir model base mechanism.

Table 2. Isotherm model parameters from toluene adsorption regression analysis at T=20°C

Isotherm	***Equation***	***Parameter***	***Value***			**R^2**
			Mean	***Std error***	***T-test***	
Temkin	$\omega = B \cdot \ln(KC)$	*K* (m^3/mol) *B (mol/kg)*	$3.97 \cdot 10^{1}$ $2.61 \cdot 10^{-1}$	$1.58 \cdot 10^{1}$ $2.91 \cdot 10^{-2}$	2.52 9.03	0.901
Freundlich:	$\omega = k \cdot C^n$	*K* (mol/kg)/(mol/m^3)^n *n*	6.72 $4.47 \cdot 10^{-1}$	$5.98 \cdot 10^{-2}$ $2.20 \cdot 10^{-2}$	11.25 20.35	0.989
Langmuir:	$\omega = \frac{\omega_{\max} K \cdot C}{1 + K \cdot C}$	ω_{max} (mol/kg) *ΔG* (kJ/mol) *K* (m^3/mol)	1.83 - $1.12 \cdot 10^{1}$ $9.80 \cdot 10^{1}$	$1.94 \cdot 10^{-1}$ 2.4 2972	9.43 18.52 3.58	0.941
Langmuir-Freundlich:	$\omega = \frac{\omega_{\max} (K \cdot C)^n}{1 + (K \cdot C)^n}$	ω_{max} (mol/kg) *K* (m^3/mol) *n*	$1.92 \cdot 10^{2}$ $3.54 \cdot 10^{-2}$ $4.49 \cdot 10^{-1}$	$8.21 \cdot 10^{3}$ 1.53 $2.74 \cdot 10^{1}$	0.23 0.23 4.88	0.989
Dubinin-Radushkevich:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^2 \right]$	ω_{max} (mol/kg) *E* (kJ/mol)	3.57 $1.31 \cdot 10^{4}$	1.84 $3.33 \cdot 10^{3}$	1.94 3.93	0.978
Dubinin-Astakhov:	$\omega = \omega_{MAX} \exp\left[-\left(\frac{RT}{E} \ln\left(\frac{c_s}{c} \right) \right)^n \right]$	ω_{max} (mol/kg) *E* (kJ/mol) *n*	$1.41 \cdot 10^{2}$ $8.17 \cdot 10^{2}$ $5.55 \cdot 10^{-1}$	$5.86 \cdot 10^{2}$ $3.16 \cdot 10^{3}$ $4.53 \cdot 10^{-1}$	0.24 0.26 1.23	0.991

Hence, for toluene data modelling, the Freundlich model can be successfully used (Figure 1 B), also considering that the other models selected show very high uncertainty in parameter estimation, as their high relative standard errors confirm.

For a deeper analysis of benzene/toluene adsorption mechanism, a binary test was carried out, also to test the occurrence of competition phenomena during their simultaneous adsorption on the same activated carbon. As discussed above, benzene and toluene are expected to adsorb according the same mechanism, but adsorption phenomena strictly depend on analyte concentrations, hence the behaviour of the binary system cannot be easily predicted.

Figure 3 reports the experimental results for benzene and toluene binary adsorption. For both analytes, the corresponding single-compound adsorption isotherm at the same temperature was also included, to allow for a direct comparison. The analysis of the binary experimental data showed that toluene is adsorbed more than benzene, following the same behaviour of the corresponding single-compound systems. This result is consistent with those reported in previous works dealing with the adsorption of organic compounds from water (e.g. [21]). Moreover, a significant reduction in adsorption capacity with respect to the correspondent single-compound data was observed for both

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compounds (except for a very low concentration range for which single-compound and binary adsorption data almost overlap), indicating the competitive adsorption toward the same active sites. The interference and competition phenomena arising in these systems can be described and, sometimes predicted by specific adsorption models, whose mathematical formulation can be more or less complex, depending on the physical adsorption mechanism hypothesized. To this aim, a multicomponent Langmuir model was initially chosen for its simplicity and low number of fitting parameters, easily valuable through single-compound experimental tests [21]. The equations representing the multicomponent Langmuir adsorption model are reported in fundamental works on adsorption (e.g. [18]). The comparison between Langmuir multicomponent model and binary experimental data (not reported) provided average results until a definite AC surface coverage (approximately equal to 0.2 mmol g^{-1}). For higher values, the model was substantially inadequate for both compounds.

In order to find a valid model in the entire range of equilibrium concentrations tested, the binary experimental data were analyzed in light of the Ideal Adsorbed Solution Theory (IAST) model [22]. The IAST model provides a thermodynamically consistent method for predicting multicomponent adsorption isotherms using single-compound isotherm data.

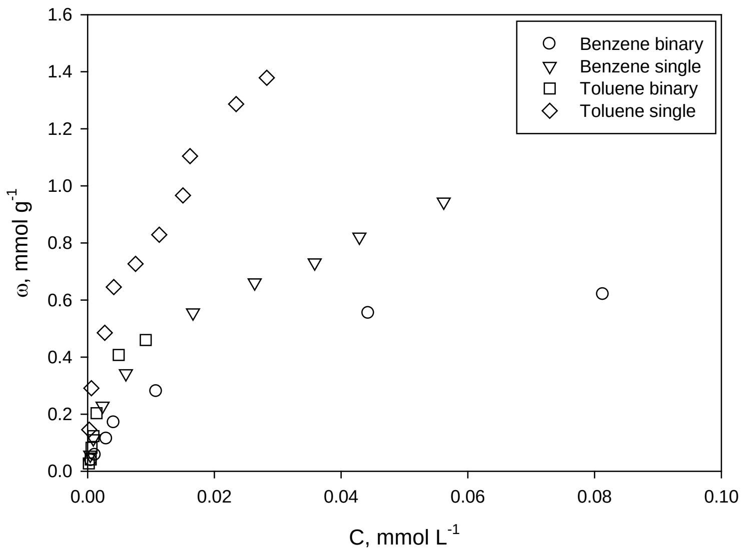


Figure 3. Benzene and toluene adsorption isotherms in binary system (1:1, on molar basis) onto F400 activated carbon. T= 20° C, equilibrium pH=8. Comparison with single-compound data

The IAST model is based on the assumption that the adsorbed mixture forms an ideal solution in equilibrium with liquid phase at a constant spreading pressure for each solute (π_i), in analogy with Raoult's law for vapour–liquid equilibria. Moreover, it hypothesizes a reduction in adsorption capacity of both compounds in binary systems with respect to their single-compound counterpart, and proportional to the latter. In IAST model, the following five basic equations are used to predict multicomponent adsorption capacity from the corresponding single-compound data:

$$C_i = C_i^0(T,P,\pi)\cdot z_i \quad \text{i=1...N} \tag{2}$$

$$z_i = \frac{\omega_i}{\omega_T} \quad \text{i =1...N} \tag{3}$$

$$\omega_T = \sum_{i=1}^{N}\omega_i \tag{4}$$

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$$\frac{1}{\omega_T} = \sum_i \frac{z_i}{\omega_i^0} \quad \text{i =1…N} \tag{5}$$

$$\pi_i(C_i^0) = \frac{RT}{A} \cdot \int_0^{C_i^0} \frac{\omega_i^0(C_i^0)}{C_i^0} dC_i^0 \quad \text{i =1…N} \tag{6}$$

Where:

- C_i is the equilibrium liquid concentration of adsorbates in a multicomponent system;
- C_i^0 is the equilibrium liquid concentration of adsorbates in a single-compound system;
- ω_i^0 is the single-compound adsorption capacity calculated, at same pressure, temperature and spreading pressure of the multicomponent system;
- z_i, is the mole fraction of each compound on carbon surface;
- ω_T is the total surface loading, i.e. the sum of solutes adsorption capacities (ω_i) in the multicomponent system;
- A is the specific adsorbent area;
- R is the universal gas constant;
- T is the absolute temperature.

Further details on IAST model are reported in Erto et al. [21]. The application of the model requires an appropriate single-compound adsorption model, so as to allow a reliable prediction of multicomponent adsorption data. In this work, the Langmuir equation parameters obtained from the single-compound systems (Tables 1-2) were used as they provided the best comparative results. In Figure 4, the results of the IAST modelling analysis are reported.

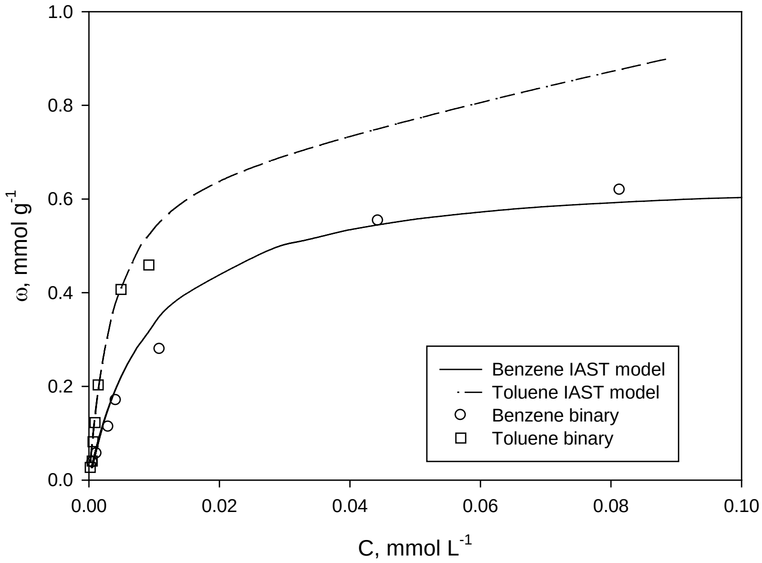


Figure 4. Modelling of benzene/toluene binary adsorption system (C^0_{ben}:C^0_{tol} = 1:1) by IAST model

It can be observed that the modelling results are very satisfying for both compounds, as the adsorption capacity is correctly predicted on the entire range of equilibrium liquid concentrations tested, as requested. It can be deduced that the binary system tested has an ideal behaviour under the experimental conditions adopted; hence, the interactions between the adsorbed molecules can be considered as negligible. This result is in line with the adsorption mechanism derived from the thermodynamic analysis reported above. Actually, even if for toluene the presence of lateral interactions can be reasonably expected also in binary system, their occurrence can be neglected because of the lower equilibrium concentrations tested, which in turn are due to its significantly

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higher adsorption capacity (cf. Figure 3). In conclusion, the IAST model is a valid tool for the prediction of adsorption data of the investigated system and the predictable character of the model allows its extension to wider experimental data, until lateral interactions between adsorbed molecules arise and determine a non-ideal behavior of the system.

4. CONCLUSIONS

The adsorption of benzene and toluene from simulated groundwater onto an activated carbon, both in single-compound and binary systems, was studied. Experimental results in single-compound systems showed that, for each temperature, toluene is adsorbed more than benzene.

The analysis of the isosteric heat of adsorption showed the existence of lateral interactions for toluene adsorbed molecules, likely due to the addition of an electron-donor functional group (i.e. methyl) to the aromatic ring. This group gives rise to a non-symmetric charge distribution, an increase in the electronegativity of the ring, stronger attractions to the nucleophilic carbon basal plane, thus influencing also the overall adsorption capacity.

The experimental data on binary system showed that toluene is adsorbed more than benzene, mirroring the same behavior as the corresponding single-compound systems. However, a significant reduction in adsorption capacity with respect to the corresponding single-compound data was observed for both compounds, which confirms there is competitive adsorption toward the same active sites. Finally, very good data prediction can be obtained by IAST model in the entire range of the equilibrium concentrations tested.

References

[1] Mitra, S., Roy, P., 2011. BTEX: a serious groundwater contaminant. *Res. J. Environ. Sci.*, **5**, 394-398.

[2] Bortone, I., Erto, A., Santonastaso, G., Di Nardo, A., Di Natale, M., Musmarra, D., 2015. Design of Permeable Adsorptive Barriers (PAB) for groundwater remediation by COMSOL Multi-physics simulations. *Desalin. Water Treat.*, **55(12)**, 3231-3240.

[3] Agency for Toxic Substances and Disease Registry (ATSDR), 2007. Toxicological Profile for Benzene (Draft), U.S. Department of Health and Human Services, Atlanta, GA.

[4] Liang, C., Chen, Y.J., 2010. Evaluation of activated carbon for remediating benzene contamination: adsorption and oxidative regeneration. *J. Hazard. Mater.*, **182**, 544-551.

[5] Bortone, I., Di Nardo, A., Di Natale, M., Erto, A., Musmarra, D., Santonastaso, G.F, 2013. Remediation of an aquifer polluted with dissolved tetrachloroethylene by an array of wells filled with activated carbon. *J. Hazard. Mater*, **260**, 914-920.

[6] Erto, A., Di Natale, F., Musmarra, D., Lancia, A., 2015. Modeling of single and competitive adsorption of cadmium and zinc onto activated carbon. *Adsorption*, **21(8)**, 611-621.

[7] Erto, A., Bortone, I., Di Nardo, A., Di Natale, M., Musmarra, D., 2014. Permeable Adsorptive Barrier (PAB) for the remediation of groundwater simultaneously contaminated by some chlorinated organic compounds. *J. Environ. Manage.*, **140**, 111-119.

[8] Yu, M., Hunter, J.T., Falconer, J.L., Noble, R.D., 2006. Adsorption of benzene mixtures on silicate-1 and NaX zeolites. *Micropor. Mesopor. Mater.*, **96**, 376-385.

[9] Chin, C.J.M., Shih, M.W., Tsai, H.J., 2010. Adsorption of nonpolar benzene derivatives on single walled carbon nanotubes. *Appl. Surf. Sci.*, **256**, 6035-6039.

[10] Akthar, M., Hasany, S.M., Bhanger M.I., Iqbal, S., 2007. Sorption potential of Moringa Oleifera pods for the removal of organic pollutants from aqueous solutions. *J. Hazard. Mater.*, **141**, 546-556.

[11] Alamo-Nole, L.A., Perales-Perez, O., Roman-Velazquez, F.R., 2011. Sorption study of toluene and xylene in aqueous solutions by recycled tires. *J. Hazard. Mater.*, **185**, 107-111.

[12] Best Available Techniques (BAT) Reference Document for Waste Treatment, 2015 – European Commission - Industrial Emissions Directive 2010/75/EU.

[13] Radovic, L.R., Moreno-Castilla, C., Rivera-Utrilla, J., 2001. *Carbon materials as adsorbents in aqueous solutions. In Chemistry and Physics of Carbon*, Marcel Dekker, New York.

[14] Villacañas, F., Pereira, M.F.R., Orfao, J.J.M., Figueiredo, J.L., 2006. Adsorption of simple aromatic compounds on activated carbons. *J. Coll. Interf. Sci.*, **293**, 128-136.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[15] Li, L., Quinlivan, P., Knappe, D.R., 2002. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon*, **40**, 2085-2100.
[16] Balsamo, M., Rodriguez-Reinoso, F., Montagnaro, F., Lancia, A., Erto, A., 2013. Highlighting the role of activated carbon particle size on CO_2 capture from model flue-gas. *Ind. Eng. Chem. Res.*, **52**, 12183−12191.
[17] Erto, A., Andreozzi, R., Di Natale, F., Lancia, A., Musmarra, D., 2010. Experimental and statistical analysis of trichloroethylene adsorption onto activated carbon. *Chem. Eng. J.*, **156**, 353-359.
[18] Suzuki M., 1990. *Adsorption Engineering*. Elsevier, Amsterdam
[19] Wibowo, N., Setyadhi, L., Wibowo, D., Setiawan, J., Ismadji, S., 2007. Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption. *J. Hazard. Mater.*, **146**, 237-242.
[20] Kleineidam, S., Schuth, C., Grathwohl, P., 2002. Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants. *Environ. Sci. Technol.*, **36**, 4689-4697
[21] Erto, A., Lancia, A., Musmarra, D., 2011. A modelling analysis of PCE/TCE mixture adsorption based on Ideal Adsorbed Solution Theory. *Sep. Purif. Technol.*, **80**, 140-147.
[22] Radke, S.J., Prausnitz, J.M., 1972. Thermodynamics of multi-solute adsorption from dilute liquid solutions. *AIChe J.*, **18(4),** 761-768.

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Environmental Aspects of Marinas and Touristical Ports

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Greek marinas: a mythical saga

G. E. Andrianis[*], E. G. Andrianis

Triton Consultants (Cyprus) Ltd, 18 Kyriakou Matsi, 2408, Engomi, Nicosia, Cyprus.
*Corresponding author: Email: gandrianis@tritonconsultants.eu

Abstract

Greece, a country of a 16,000km long coastline and hundreds of islands and islets, boasts herself for being a leader in coastal and marine tourism due to the numerous summer visitors of its islands. The mere number alone, 22 only, of the organized marinas situated in Greece is a significant indicator of the country's underperformance in the yachting/boating/marinas area, a vital and increasingly popular, internationally, subcategory of marine tourism. While a marina per island approach may not be a financially viable and environmentally sound approach, a closer look at the Greek permitting and licensing procedures and regulations reveals a heavily bureaucratic and time consuming procedure masked under the premises of environmental protection, which prevents even a more structured and organized marina/harbor/anchorage scheme. Water related (dredging, construction of piers and breakwaters etc.) and land related impacts (run-off into wetlands, lost land use, dust etc.) are unavoidable but modern technologies and innovation have yet to be implemented in the outdated laws and required procedures. For Greece to remain competitive in the marina tourism industry, the challenge is to simplify the procedures which cause delays and set obstacles at no expense however of the environment and landscape which is the single most important reason for Greece's leading place in the global tourist scene.

Keywords: marinas; marine tourism; licensing procedure

1. INTRODUCTION

Tourism has traditionally been one of the Greek economy's driving forces, as is confirmed by the Travel and Tourism sectors' contribution to the Gross Domestic Product (GDP) for the years 2000-2013, which was approximately 17%. (Source: SETE, August 2014 based on data provided by the Bank of Greece and the World Travel & Tourism Council). The reasons people chose to travel for vacation varies with some of the main categories being nature, culture, city trips, sports-related activities, specific events but almost half (46%) of the Europeans who traveled in 2013 did so, to visit destinations where sun/beach prevail (Source: Flash Eurobarometer 392). For a country like Greece which is being regarded as one of the top summer destinations worldwide, it is reasonable to assume that marine tourism, and marinas in particular, would constitute a significant role in the country's growth efforts. While steps have been taken towards this direction, Greece still lags behind some of its main competitors in marine tourism, with the permitting and licensing procedures for marinas requiring feedback from numerous public agencies and significant time which in many cases discourage any investors to proceed with any new marina developments. One of the main reasons that permit issuance is usually delayed is attributed to environmental issues which in some, but not all cases, may be justified. However a study of the main environmental challenges posed in port, harbor and marina construction suggests that the bureaucracy involved around such matters and the number of stakeholders in charge of providing consent for approval is the main source of delay and/or annulment of new marina projects and not the environmental concerns. While it is important to preserve, Greece's natural landscape, which is along with its

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weather, the most important reason for attracting tourists, this does not mean it has to be done at the expense of new marinas' development and hence the environmental protection laws that exist need to be enhanced through a modernized, simplified permitting procedure.

2. DEFINITION OF RECREATIONAL/TOURIST PORTS ACCORDING TO GREEK LEGISLATURE

According to Act no. 4070/Government Gazette Volume A, Sheet Number 82/April 10th 2012, Article 156 [1], "Tourist Port" for recreational vessels is the land and sea area which is intended as a primary reason for/and to support functionally the berthing of recreational and watersport vessels. "Tourist Ports" comprise of marinas, boat shelters and anchorages.

Marina is the "tourist port" which provides land and water infrastructure for the service of vessels and their users according to the specifications defined in the Ministry of Culture and Tourism's resolution.

Boat shelter is the "tourist port" with basic building facilities of a minimum plan area for the port authorities of $100m^2$ which provisions and services for water, power, communications, fuel supply, slops and trash collection, fire fighting, accommodation and basic hygiene.

Anhoarage is the "tourist port" which is formed within sheltered havens, lakes and rivers for a limited number of berths with light equipment which does not have permanent impact on the environment and fundamental infrastructure.

Based on the definitions above Greece has only 22 marinas (and an additional one located in the Mesolonghi lagoon) for a coastline of approximately 16000km. Even though this figure may be slightly deceiving due to the numerous uninhabited islands and islets of numerous sizes, the number of marinas for an island nation is considered to be very small and at the same time very limiting for the potential growth of the marine tourism industry. Comparing Greece's marina infrastructure to that of its two main competitors (Table 1) the country's underperformance in this sector of the tourism economy is evident, as countries with less than half of Greece's coastline length have twice as many marinas and number of berths.

Table 1: Croatia-Turkey-Greece, Comparison of Marinas and Berths

Country	Coastline (km) [2]	Number of Marinas	Number of Berths
Croatia	5835	56	~16000
Turkey	7200	43	>13121
Greece	16000	22	~8000

Greece has a great potential of growth in marine tourism due to the plethora of major islands at very close distances. Nowadays the Athens Riviera marinas are the main bases for sailing boat cruises which are currently limited to a 7-day to their vast majority. Development of more island marinas can extend the duration of these cruises to bring visitors to more islands as suggested in Figure 1. It is understood that the one-marina-per-island model may not be an economically viable solution but a careful study of the island network can provide an overall master plan for the development of more marinas.

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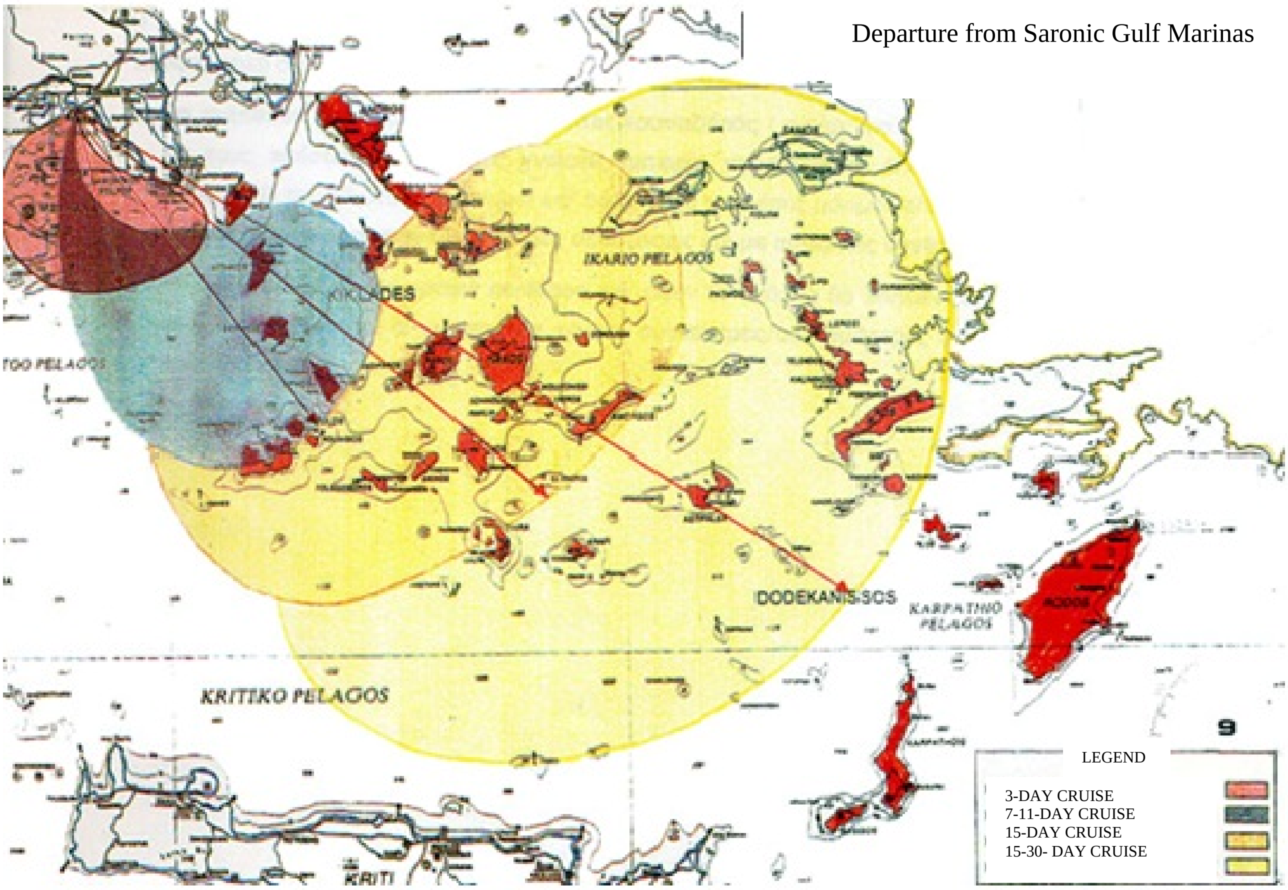


Figure 1: Multiple-day Cruise Potential in the Central Aegean Sea

3. ENVIRONMENTAL ISSUES FOR THE DEVELOPMENT OF MARINAS

Any type of construction is anticipated to have impacts (greater or lesser) to the environment and it is mainly the engineers' responsibility to mitigate them. Identifying the potential impacts is a very critical step in the design process and the meticulous study of the local conditions is very important. The experience has shown that developments can have serious implications for many aspects of the environment. Because of the nature of maritime works, a wide range of very different environmental activities are likely to be affected in one way or another, many of these permanently.
Developments require sound management of natural resources, particularly renewable resources, and systematic attention to their impact on the environment. Renewable resources include living resources (plants, animals and fishes) and other natural resources (particularly soils and water) that create or sustain life and that are self-renewing if not mismanaged. However, some general environmental issues exist which can be addressed early on irrespective of the location and they have been described in Wolrd Bank's Technical Paper Number 126 Transport and the Environment Series, "Environmental Considerations for Port and Harbor Developments" [3]. Marinas in many cases involve lighter structures, such as floating pontoons, when compared to gravity type structures, and therefore have a smaller environmental impact but issues are common for any marine facility and the most critical are described below.

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3.1 Water Related Impacts

3.1.1 Impacts caused by dredging

Dredging, whether be it for the formation of navigation channels or for the general dredging of the basin may be problematic due to the dispersal and settlement of resuspended sediments on sensitive aquatic ecosystems. For this reason in Greece a permit to reintroduce the dredged material in areas with sea depth of over 50m is required and in some cases the dredged materials have to be transported and disposed on land which can be a very costly operation.

3.1.2 Construction of piers, breakwaters and other structures

The construction of gravity type structures provide the biggest problems which mainly consist of erosion and accretion effects when such structures are in zones of high littoral sediment transport. Sediment bypassing arrangements may be considered to preserve downdrift coastlines and also care needs to be taken in closely-formed basins which if not properly designed (through the use of mathematical modes or physical models for example) then difficult sea conditions which may affecting the berthing boats may develop.

3.1.3 Ship discharges-bilge water-sewage

To prevent vessels from discharging oily and bilge water as well as sewage in an unorganized manner which can result to pollution of the marine environment, modern marinas are required to provide facilities to receive wastes from the berthed vessels.
In marine environmental impacts, there is very often the need for monitoring of water quality and the sea floor by marine biologists and other specialists. This monitoring should be commenced during the preparation stage and continued in many cases long after the completion of the project.

3.2 Land Related Impacts

3.2.1 Relocation; lost land use; involuntary resettlement

There are many instances where marina development need to relocate an existing village, or a fishermen's beach or agricultural lands. An acceptable resettlement plan will have to be made an integral part of the project. Socio-economic studies are commenced as soon as project design since resettlement can be more complicated than the project engineering and very time consuming. In such a case where resettlement may be mandatory, the goal is for the resettling population to be better off under the new circumstances.

3.2.2 Dust and other airborne emissions

Wind blown dust from bulk materials stockpiles during construction as well as the traffic from the construction vehicles may cause temporary environmental issues which need to be addressed in order to minimize the effect on the surrounding population.

3.2.3 Waterfront Drainage

Modern design practices dictate the slope of any quay to designed in a way to avoid discharge of stormwater or any spill material into the marina waters, a provision which was not in place in older port and harbor designs. The stormwater is preferable to be collected and to be passed through an oil-water separator before being discharged.

3.3 Classification of Marina Environmental Impacts

The environmental impacts likely to result from marina developments, can be further classified as follows:

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3.3.1 Impacts resulting from the construction activity

These commence usually as soon as construction has been launched.
However, impacts may persist beyond the construction period especially if they result from unnecessarily disruptive or careless engineering /construction practices.

3.3.2 Operational impacts – there are three categories

i) Those that are losses or degradation of the environment and result from some alteration (frequently irreversible) attributable to the project;
ii) Those that are not necessarily irreversible but persist as long as the project continues to operate and the related activities continue; and
iii) Those resulting from the decommissioning of redundant facilities coupled with the need to rehabilitate the affected areas to an acceptable environment standard.

As discussed in this section various environmental impacts do exist in marinas development that need to be identified and considered. However, experience and knowledge that has been gained (and which has also been incorporated into legislature) proves that these impacts can be addressed in the design of a certain project. The existence of environmental impacts, as these are identified in the required Environmental Impact Assessment Study, should not be the basis for a cancellation of a development/investment but rather it shall form the basis for addressing efficiently these potential impacts. Figures 2-4 depict successful examples of marinas development of various sizes and for the accommodation of different types of vessels (sailing boats vs. Mega yachts for example) both is an urban and rural environment which proves that with the proper design and consideration of the surrounding natural environment, solutions can be available. In many instances, as in the case of Athens Marina (Figure 2), the development of marina may lead to an upgrade of an entire plot of land. Prior to the construction of the marina in Neo Faliro the beach front area was a rarely visited area full of trash being washed off at its shore.



Figure 2: Athens Marina (former Faliro Marina). The construction of the marina for super yachts led to an upgrade of the area which was prior a rarely visited sea shore full of debris

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Figure 3: Olympic Marine mainly comprising of floating pontoons, Lavrio


Figure 4: Porto Karras Marina. The marina with berths predominantly comprising of floating pontoons blends in harmonically with the picturesque Chalkidiki landscape

4. PROCEDURE FOR MARINE TOURIST INFRASTRUCTURE ACCORDING TO THE LEGISLATION (ACT 2971/19.12.2001 [4], ACT 3201/2003 [5] & ACT 2160/19.07.1993[6])

The following paragraphs summarize the required procedures to obtain a permit for the development of a marina in Greece.

4.1 Permitting procedures according to article 14 of the legislation Act 2971/19.12.2001 (government gazette 285A') and as amended by Act 2301/2003 for marina outside port authority zone.

The procedure under the title is only applicable only if the plot that will be developed has been conceded (as dictated by law).

a) In this case the interested party files an application to the Land Department in charge which includes a Technical Dossier.
b) The Land Department transmits within one (1) month, the relevant file to the following recipients in order to express their legal opinion for the issues within their jurisdiction within three (3) months.

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1. Ministry of the Environment and Energy, Directorate of Environmental Licensing (DI.P.A.) or the Environmental Commission of the relevant Prefecture. Three (3) copies for the pre-approval of the location.
2. Hellenic Navy General Staff (two copies)
3. Ministry of Shipping and Island Policy
4. Planning and Environment Commission of the relevant Prefecture
5. Ministry of Culture and Tourism (three copies)
6. Greek Tourism Organization
7. Municipal Board of the relevant Municipality
8. Ministry of Economy, Development and Tourism

c) Following the location pre-approval as per [7] and the expression of legal opinions of the case (b) above, the Environmental Impact Assessment Study is submitted and approved as per applicable legislation. Following the opinions by the Hellenic Navy General Staff (for issues pertaining to national defense and navigation safety), by the Ministry of Shiping (for reasons pertaining to rational marine development, coastline protection, control and safeguarding of navigation and transportation) and of the Ministry of Culture (for reasons pertaining to the protection of antiquities) the final design is approved in which the approved environmental conditions have to be accounted for. Legal opinions on the final design are to be submitted within a three (3) month period. The approved Final Design with the legal opinions described above is transmitted to the Land Department in charge for the concession approval.

By way of the decision of the Ministers of Finances, Economy, Development and Tourism, Infrastructure, Transport and Networks, Environment and Energy, and of the Ministry of Shipping and Island Policy which is issued following a proposition by the Ministry of Economy, Development and Tourism following the legal opinionof the Committee of Public Plots, on which particularly for this case a representative of the proposing Ministry is sitting, it is allowed to proceed to a concession following a public competition of the rights to use the beach, sea or sea bottom and its subsoil to those who have founded or have the intention to found, in private plots which they own or have the right to use for marine tourist infrastructures.

4.2 Permitting for works within the port zone or a port authority

For the execution of works the following are prerequisites:

a) Ruling of the Executive Board of the managing authority.
b) Compatibility check with the approved, by the Commission of Planning and Development of Ports Master Plan. The permitting procedure is not impeded by the non-completion of the Port's Master Plan update until the end of the deadline set on paragraph 5β, Article 44 of the legislation act 4150 [8] .
c) Approval of the Environmental Conditions as per legislation act 4014/2011 (A' 209) as valid. If the works belong to subcategory A1 in Article 3 of legislation act 014/2011, the deadlines provisioned in paragraph 2 in Article 3 of legislation Act 014/2011 and which are over five (5) and below fifteen (15) working days, are shortened by five (5) working days whereas the remaining are shortened by ten (10) working days.
d) Ruling of the Ministry of Shipping and Island Policy, which acts asa construction permit for the works. This ruling is issued within fifteen (15) days from the submittal of the relevant application from the managing authority, accompanied by the (a) and (b) above.
e) For the commencement of the works, the ruling described in (d) above needs to be notified to the local Coast Guard Authority.
f) For works under a concession status, the concessionee is legitimized, if the relevant agreement provisions it, to submit the application for the construction permit issuance to the Ministry of Economy, Development and Tourism, instead of the Port's Managing Authority.

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g) Construction works executed within Ports Authorities, and in the event which are not under the agreement overseen by the relevant Port Authority, are overseen by the General Secretariat for Ports, Ports Policy and Marine Investments of the Ministry of Marine and Island Policy. The oversight is performed either directly by the services of the Secretariat or from the Secretariat through the commissioning of independent firms with the procedures provisioned in the agreement.

4.3 Permitting of works administered by the Hellenic Republic Asset Development Fund (HRADF)

Different legislature is in effect for concessions performed by HRADF depending on the Concession Terms of the Agreement and the provisioned in the Agreement clauses for the property in question for marine touristic infrastructures.

4.4 Overview

It is evident that, regardless of the permitting procedure that needs to be followed depending on the location of the proposed development, any marina proposal is a rather complex and time consuming process which poses more obstacles than many of the environmental impacts combined. A simplification of the licensing and permitting procedure does not mean a relaxation in the environmental concerns which are addressed, regardless, in the required by law in the Environmental Impact Assessment Study.

5. CONCLUSIONS

Environmental protection in the cases of marinas development, just like in any other engineering project, can be achieved through the mitigation of the environmental impacts identified during the design stage. A complex and lengthy permitting and licensing procedure does not safeguard the protection of the environment in the areas where marinas are proposed to be developed. A new simplified approach in the licensing procedure is required to provide the grounds for the development of new marinas which will help improve the existing level of marine tourism services and grow it further to compete with neighbouring countries.

References

[1] Act 4070/10.04.2012, Government Gazette Volume A, Sheet Number 82, Article 156, Legislation Ammendment for the Development and Operation of Tourist Ports and Other Provisions

[2] *The World Factbook* 2013-14. Washington, DC: Central Intelligence Agency, 2013

[3] John D. Davis, Scott MacKnight, IMO Staff, and Others, 1990, World Bank Technical Paper Number 126, Trasnport and the Environment Series, Environmental Considerations for Port and Harbor Development, The World Bank, Washington, D.C. 20433, U.S.A.

[4] Act 2971/19.12.2001, Government Gazette 285A, Seashore, Beach and Other Provisions

[5] Act 3201/05.12.2003, Government Gazette 282A Restoration, Protection and Enhancement of the Natural and Artificial Environment of the islands under the jurisdiction of the Ministry of the Aegean

[6] Act 2160/19.07.1993, Government Gazette A’118, Tourism Regulations and Other Provisions

[7] Act 4179/08.08.2013, Government Gazette 175, Procedural Simplification for the Enhancement of Tourism Entrepreneurship , Reorganization of the Greek Tourism Organization and Other Provisions.

[8] Act 4150/29.04.2013, Government Gazette A/102, Restructuring of the Ministry of Shipping and The Aegean Sea and Other Provisions.

Dredging and sediment management in marinas and touristical ports

G. Papacharalampous

Civil Engineer, Postgraduate Student, Department of Civil Engineering,
National Technical University of Athens, 15780 Athens, Greece.
Email: papacharalampous.georgia@gmail.com

Abstract

Best practices in the field of dredging and sediment management in marinas and touristic ports are outlined. Integrating dredged material management as an integral aspect of resource management is of major importance. For that, a hierarchical model for dredged material management options according to the widely adopted waste hierarchy model is presented. Minimizing the volumes of sediments that must be dredged is vital. This commonsense approach is environmentally friendly and will also generate significant economic benefits. The present paper highlights this fact and introduces new insights into dredged material management in marinas and touristic ports reviewing the literature.

Keywords: integrated dredged material management; prevention; sediment management; contamination control; natural resources

1. INTRODUCTION

Marinas and touristic ports have some specific characteristics that create additional problems to those of larger commercial ports regarding dredging and dredged material management. For example, marinas are always constructed to be protected as much as possible from wave action, thus there is a greater chance of sedimentation in their basins. Another consideration for marinas and touristic ports that additionally intensifies the need for maintenance dredging and also incommodes the process of dredging is the maximum use of available space, thus the narrowness of space inside them as also the formation of zones where flow rates are very low [5].

Although the awareness of environmental protection and better management of natural resources is increasing worldwide, the environmental impact due to dredging and dredged material operations is often serious. The expenses are also high and recurring. Within an Integrated Coastal Zone Management, new approaches for sediment management need to be considered by the scientific community and local stakeholders. Emphasis should be put on the fact that dredged material can be managed by eliminating or reducing the need for initial, maintenance and environmental dredging [5, 7, 9].

This present paper presents research in the field of dredging and sediment management in marinas and touristic ports reviewing the literature. In Section 2 a hierarchy model for dredged sediments management is presented and the terms involved in this particular model are briefly described. In Sections 3 and 4 best practices for the reduction of sedimentation and sediment pollution in marinas and touristic ports are outlined respectively. In Section 5 the main conclusions reached are summarized.

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2. INTEGRATED DREDGED MATERIAL MANAGEMENT

An inverted pyramid hierarchy model for dredged material management options in accordance with the widely adopted waste hierarchy model [2] is presented in the figure below (Figure 1).

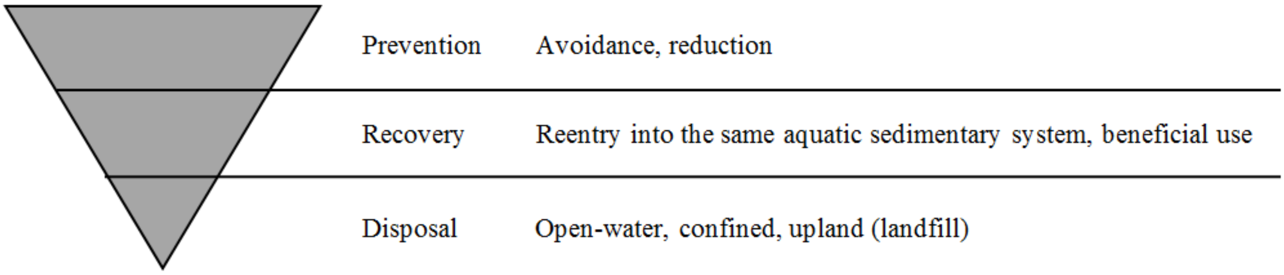


Figure 1. Hierarchy of dredged material management options.

Dredging prevention, the top of dredged material management hierarchy, can be achieved by adopting best practices for minimizing the need for dredging during both port construction and operational phases. The reduction of sedimentation in port facilities is essential for reducing the need of maintenance dredging and therefore its environmental and economic impact, as also for keeping sediments in their natural sedimentary system. New engineering solutions and technologies will have to be mobilized for this specific purpose. The optimization of the port's layout, including its entrance, plays a vital role in controlling sedimentation [5, 9].

Source control of contaminant inflow into ports' basins is another important consideration [1, 6, 7, 11]. By reducing sediment pollution the need for environmental dredging is minimized. In addition to that, unpolluted to slightly polluted dredged material can be reentered into the same aquatic sedimentary system or beneficially used (i.e., for engineering, environmental and agricultural purposes) without previous treatment in both cases. Those natural recovery options yield highly desirable outcomes in environmental as also in economic terms.

Dredged sediments are recognized as part of the natural sediment cycle [7] and therefore their reentry into the same aquatic sedimentary system is more desirable than any other recovery option. Concerning the beneficial use of dredged sediments, the feasibility of the related options depends significantly on their grain size distribution and more specifically on their percentage of coarse-grained fraction, which is considered essential to be high. The availability of beneficial uses for the coarse-grained fraction that make financial sense in the surrounding area is also crucial [8].

There is a big list of beneficial uses of dredged sediments [7], which should be evaluated in relation to the contaminant load associated with the coarse-grained fraction [8]. Regarding contaminated sediments that cannot be beneficially used directly, decision making will require comparative risk assessment, cost-benefit analysis and life cycle assessment [3, 4]. Treatment in order to make contaminated dredged material suitable for beneficial use is in this case the most desirable option [7], though it can be environmentally and/or economically unviable and thus avoided. The choice of the remediation technique is guided by the considerations of suitability and accuracy of technology in the light of sustainability principles [12].

Disposal of dredged sediments is the least desirable option and has to be prevented by adopting best practices during port construction and operation. Dredged sediments disposal signifies their exit from the sedimentary cycle. One disposal option is their placement at a suitable location in the neighboring open-water area. Previous treatment may be required for environmental and economic reasons. As a matter of fact, the increasing interest on sediment contamination treatment techniques stems from the potential economic damage from contaminated sediments [12]. Other disposal

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options are confined (aquatic or land) disposal and disposal in landfills (upland disposal). For dredged sediments classified as toxic there is a requirement for disposal in a hazardous waste landfill [8]. Dumping in the open-water area, a common practice in the past, is nowadays strictly prohibited.

Although dredged material management has gone through significant developments over the last decades, there is still large room for improvement. For that, a mind shift is considered as necessary. Prevention is the key [2].

3. REDUCING SEDIMENTATION IN MARINAS AND TOURISTIC PORTS

As already discussed in the previous section, environmental and economic problems inseparable from dredging activities can be prevented by reducing sedimentation within the marinas' and touristic ports' basins. For this purpose, a various range of engineering approaches are available. Solutions tend to be unique for each port, as they depend on its layout, the wave climate and sediment type and supply [9]. Physical or mathematical models constitute helpful tools for the investigation of sediment transport and sedimentation processes and thus for the evaluation of different options [5]. Engineering experience is exceptionally valuable in this assessment.

There is a causal relationship between hydrodynamics and sediment transport. Therefore, the selection of port locations of low wave energy potential, e.g. within natural bays, is crucial for the achievement of low maintenance costs, as also for the elimination of shoreline erosion downdrift of the port [5]. Otherwise, more expensive alternatives for the reduction of sedimentation can be followed. Sediment bypass of the port can occur through the land area in the rear of the port either through the sea area in front of its entrance. In the second case, the optimization of the position and geometric characteristics of the entrance is required, so sediment's entry in the marina or the touristic port is prevented [5, 9].

The overall optimization of the port's layout is essential for keeping sediment that enters the basin moving and thus reducing sedimentation, while the requirements of calm wave conditions in berth positions are also met. Renewal pipelines, structural elements that train natural flows and other kind of designs [9] can be used for this specific purpose. At this point, the occurrence of sedimentation problems within the Venetian Harbour of Chania, Greece since the closure of an old pipeline constructed for the port water renewal is perhaps worth mentioning (Figure 2).



Figure 2. Sedimentation problems in the Venetian Harbour of Chania, Greece.

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Other engineering solutions, such as the construction of sediment traps in front of the port's entrance and the use of mechanical equipment for the generation of flows with appropriate intensity, may have effect on keeping the sediment out or keeping it moving within the marina's basin [5, 9]. In any case, it is of importance to recognize that reducing sedimentation in a port's basin is a complex and unique hydraulic engineering problem to be solved and hence a great challenge for port engineers.

4. REDUCING SEDIMENT POLLUTION IN MARINAS AND TOURISTIC PORTS

Reducing sediment pollution in marinas and touristic ports can also bring significant environmental and economic benefits concerning dredging activities. Keeping marina's waters clean is of pivotal importance for the viability of the investment. Consequently, water and sediment pollution in marinas and touristic ports, as a sequence of both past and present day inputs, constitutes a severe problem that requires systematic approach to its management. High priority should be given to the identification and control of the main sources of contamination [1, 11], as also to better water renewal in the basins.

Sources of contamination may include storm water runoff pollution (non-point sources), industrial and domestic discharges and accidental pollution (point sources) [7]. Watershed-based sources are considered to constitute the predominant category of contamination sources [11]. As storm water flows over the land surface, it picks up potential pollutants that may include sediment, nutrients and pesticides (from agriculture), bacteria (from livestock and domestic waste), metals (from domestic waste, cities and roadways) and petroleum by-products (from vehicles) [13]. Water runoff can also carry pollutants from marinas' parking lots and maintenance areas. Accidental pollution such as fuel or waste water spills may also occur within the borders of a marina or a touristic port [6].

In literature special attention is given to organotin and organic compounds in marinas' waters and sediments [10]. Tributyltin (TBT), an organotin compound, was extensively used for approximately four decades as anti-fouling paint for boats' bottoms. Despite the strict bans on TBT-use due to its high toxicity to a wide range of organisms [14], it is disappointing to see that high concentrations persist in the sediments [10], continuing to contaminate the water column [12]. Evidently, historic contamination sources influence the sediment quality for many years after their removal [[10]].

5. CONCLUSIONS

Marinas and touristic ports have some specific characteristics that create additional problems regarding dredging and dredged material management. Minimizing the need for dredging is vital. This can be achieved by adopting best practices for the reduction of sedimentation and sediment pollution in their basins during both port construction and operational phases. The reduction of sedimentation is a unique for each port and complex hydraulic engineering problem to be solved and thus a great challenge for port engineers. Physical and mathematical models are helpful tools in the design process, while engineering experience is exceptionally valuable. Source control of contaminant inflows in the marinas' basins is also required. The approach outlined is environmentally friendly and will also generate significant economic benefits.

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References

[1] Environmental Protection Agency (EPA), 1993. *Coastal Zone Act Reauthorization Amendments (CZARA), Management measures for marinas and recreational boating*, U.S.A, pp. 1 - 9.
[2] International Solid Waste Association (ISWA), 2011. *Key issue paper on waste prevention, waste minimization and resource management*, Vienna, Austria, pp. 1 - 14.
[3] Linkov, I., Satterstrom, F. K., Kiker, G., Seager, T. P., Bridges, T., Gardner, K. H., Rogers, S. H., Belluck, D. A., Meyer, A., 2006. Multicriteria Decision Analysis: A comprehensive decision approach for management of contaminated sediments, *Risk Analysis*, Vol. 26, No. 1, pp. 61 - 78, doi: 10.1111/j.1539-6924.2006.00713.x.
[4] Maher, A., 2004. *Development of a dredge planning and decision support tool, Final Report.* New Jersey, pp. 1 - 7.
[5] Memos C., 2015. PIANC guidelines on anti-sedimentation measures in marinas and yacht harbours, *Proceedings of the 1st PanHellenic Conference on Touristic Ports, Marinas*. October 12 - 14, Athens, Greece (in Greek), pp. 297 - 307.
[6] Missouri Department of Natural Resources, 2005. *Preventing pollution at marinas, A guide to environmental compliance and pollution prevention at marinas in Missouri*, pp. 1 - 62.
[7] OSPAR Commission, 2014. *Guidelines for the management of dredged material at sea, Agreement 2014 - 06*, pp. 1 - 39.
[8] Pantazidou, M., Katsiri, A., Reddy, K. R., 2009. Evaluating management options for the disposal of dredged sediments, *ASTM International*, Vol. 6, No. 6, pp. 1 - 14, doi: 10.1520/JAI102159.
[9] Pevey, K. C., McAnally, W. H., 2010. *Sediment Management Alternatives for the Biloxi Ports, Report to Mississippi Department of Transportation*, Mississippi, pp. 1 - 12.
[10] http://www.pianc.org (accessed April 20, 2016).
[11] Stein, E. D., Ackerman, D., Schiff, K., 2003. *Watershed-based sources of contaminants to San Pedro Bay and Marina del Rey: patterns and trends, Technical report #413*, California, pp. 1 - 3.
[12] UNIDO International Centre for Science and High Technology, 2007. *Survey of sediment remediation technologies*, Trieste, Italy, pp. 1 - 8.
[13] https://www.usgs.gov (assessed April 20, 2016).
[14] BaSECO, 2006. *Tributyltin pollution on a global scale. An overview of relevant and recent research: impacts and issues*, Southampton, U.K, pp. 1 - 9.

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Environmental impacts of marinas: review of case studies

S. Papagrigoriou*, G. Kotzageorgis, Y. Bekiaris

ENVECO S.A, 1, Perikleous Str., Maroussi, 15122, Athens, Greece.
*Corresponding author: Email: info@enveco.gr

Abstract

The assessment and evaluation as well as the prevention and mitigation of the environmental impacts during the construction and operation phase of marinas play an important role not only for the procedures of their environmental permitting but also for their environmental management. The type and magnitude of these impacts are mainly related to three main factors: a) the environmental sensitivity of the marine and the neighboring terrestrial areas b) the design and the magnitude of the main technical characteristics of the marina and c) the available technical potential to mitigate the impacts. Environmental issues should be taken into account from the early stage of marina's design. Elaboration and application of proper environmental management, environmental monitoring and risk management plans can secure the sustainable development of marinas.

Keywords: environmental impacts; environmental management; waste management; pollution prevention

1. INTRODUCTION

The main aim of the European Environmental Policy is the improvement of the environment, the protection of human health, the achievement of prudent and rational use of natural resources and the promotion of international measures to address global or regional environmental problems [1]. Marinas constitute an important feature (or infrastructure) of touristic sector, and their planning, construction and operation should fully comply with the European environmental legislation and strategy. This compliance does not only ensure the environmental permit needed for the construction and operation of a Marina, but can also contribute to the incorporation of the technical design into the natural environment. It can also enhance health and safety conditions and finally promotes marinas as environmentally friendly infrastructures. The marina market is arguably more resilient than other areas of the industry [2]. A total delivered superyacht fleet (with length more than 30m), in June 2011 came to 4,117 yachts. This means that there is an increase of 95,2% over the decade 2001-2010. As for the Mediterranean coast 520,974 berths have been recorded [3]. Most of them are found in France (226,000, 43%), Spain (130,555, 25%) and Italy (130,000, 25%). Greece participates with only 8,924 (2%) berths. Taking into account the length of the coastline per country 35.78 berths correspond for each kilometer of French coastline. The corresponding numbers for Spain, Italy and Greece are 18.97, 13.64 and 0.5. Greece hospitalizes about 17,700 yachts from which 8,000 have length more than 12m. One yacht corresponds to 621 Greek habitants while for Europe is one yacht per 164 habitants. Development of marinas is related to increase of employment. 100 berths of a marina correspond to 4.4 jobs in the marina and 100 indirect supporting jobs. Additionally, taking into account the Greek National Strategy on Shipping Development the potential of marinas development in Greece is considered very high [4].

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2. LEGISLATIVE FRAMEWORK

The cornerstone of the European Legislation related to the Environmental Impact Assessment is the Environmental Impact Assessment (EIA) Directive (2011/92/EU as amended by Directive 2014/52/EU) as well as the Strategic Environmental Assessment Directive (2001/42/EC). The common principle of both Directives is to ensure that plans, programmes and projects likely to have significant effects on the environment are made subject to an environmental assessment, prior to their approval or authorization. Consultation with the public is a key feature of environmental assessment procedures. Marinas are included in Annex II of the EIA Directive. Consequently, according to paragraph 2 of article 4 of the same Directive Member States shall determine whether marinas shall be made subject to an assessment (need of elaboration and approval of Environmental Impact Assessment Study, EIAS) in accordance with articles 5 to 10. Member States shall make that determination through (a) a case –by-case examination or (b) setting specific thresholds or criteria”. According to the Greek Legislation (Law 4014/GG209A/21.09.2011, MD 1958 /GG21B/3.01.2012) the elaboration and approval of an EIAS is needed for all marinas in Greece. EIAS for marinas of equal or more than 200 boats capacity are examined and approved by the Ministry of Environment and Energy. For marinas with capacity less than 200 boats the EIAS is examined by the Decentralized Administration in which the marina is located. According to the Greek legislation the elaboration (and submission to the competent environmental authority) of a preliminary environmental study (called as preliminary identification of environmental impacts) before the elaboration of the EIAS, is optional.

In case a Marina is located into an area which has been included into the European Ecological Network Natura 2000, then according to paragraph 3, article 6 of the Habitat Directive (92/43/EC) the marina has to undergo an “appropriate impact assessment” for the assessment of the effect it may have on the site’s conservation objectives. The Appropriate Impact Assessment Study (AIAS) has to focus on the identification, evaluation and mitigation (or/and compensation) of all impacts on the ecologically important elements (habitats, flora and fauna species of Community Interest) of the natural marine and terrestrial environment. The AIAS has to be elaborated by taking into account proper fieldwork surveys on the proposed marine and terrestrial area of the marina. This study must take into account the Birds Directive (2009/147/EC) as well as the guidance document of the European Commission “Managing Natura 2000 Sites, The provisions of article 6 of the ‘Habitats’ Directive 92/43EEC” [5]. The European Biodiversity Strategy (COM(2011) 244 final) and the Marine Strategy Framework Directive (2008/56/EC) have also to be taken into account. Greek Legislation has been harmonized with the abovementioned European legislative framework. For both the EIAS and the AIAS, contents and specifications have been issued according to the MD/GG135B/27.01.2014. The AIAS is submitted to the competent environmental authority as an annex of the EIAS. According to the European and Greek legislation environmental studies are also needed for the modification of the environmental approved design of a Marina or the renewal of its environmental permit. In Greece the duration of an environmental permit is usually set to 10 years.

3. IDENTIFICATION, ASSESSMENT AND MITIGATION OF ENVIRONMENTAL IMPACTS OF MARINAS

The type and magnitude of environmental impacts of a marine project are mainly related to the following three main factors: a) the environmental sensitivity of the marine and the neighboring terrestrial areas b) the design and magnitude of the main technical characteristics of the marina such us the marine and terrestrial area which will be occupied by technical works and supporting land uses, the capacity of marina in boats etc. c) the available technical potential to mitigate the impacts and/or restore the environment. According to these factors the environmental impacts can be

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characterized in relation to their: type (negative, neutral, positive), magnitude (significant, medium, insignificant), duration (long term - permanent, medium term, short term), reversibility (irreversible, partially reversible, reversible), capacity to be mitigated by technical means (mitigated, partially mitigated, not mitigated). Impacts can also be assessed at a local level (into the study area) or a broader level (into the broader area). Assessment or Synergistic or cumulative impact also takes place in case other (existing or already permitted) plans, works or land uses are located near the marina.

Environmental impacts are mainly classified to those related either to construction or operation phase of technical projects. The new environmental European Legislation also mentions impacts related to the decommissioning of a project. The main environmental means for which possible impacts are assessed during the construction and operation phases are the following: climate – bioclimate, geology, landscape, geomorphology and soil, surface and ground water resources, Habitats - flora and fauna of marine and terrestrial ecosystems, protected natural areas, human population, land uses and traffic, existing infrastructure, social and economic environment, atmospheric and acoustic environment and cultural - historic environment. The environmental impacts of marinas are assessed by taking into account all their accompanying installations and uses (e.g. boat repair facilities, waste water treatment installations, supporting or commercial buildings, parking areas, access roads and generated traffic, electricity generators). The elaboration of the EIAS requires the preliminary design of the project. Before or in parallel to the elaboration of the EIAS an investigation of alternative solutions has to take place, according to environmental criteria. A comparative environmental assessment of technically and economically viable design alternatives (in terms of magnitude, location or proposed technology), including the do-nothing scenario has to take place.

The main categories of environmental impacts during the construction phase of marinas are mainly related to the following environmental means: 1) geomorphology and landscape: greater impacts are expected when large marinas are located into landscapes characterized by high natural beauty and absence of human activities. The need of disposal areas (marine or terrestrial, due to earth excavations or dredging) quarries for inert or filling earth material, and construction of access roads have also to be taken into account. Proper technical design of marinas (in combination with landscape architecture) and extensive environmental restoration measures can reduce these impacts. 2) Sea water quality: Pollution of sea water can be caused due to earth works, dredging and/or pollution caused by the construction machines (oil leakages). The two first activities can increase to a high degree the suspended solids density. Use of environmentally best construction practices can reduce these problems. 3) Atmospheric and acoustic environment: impacts are related to the use of construction machines and movement of heavy vehicles. 4) Land uses: Neighboring land uses and existing traffic conditions can be affected during construction period. Special planning of construction phase can reduce these problems. 4) Natural environment – biodiversity: terrestrial and submarine vegetation as well as fauna species without capabilities of quick movement will be mostly affected. The impacts are mainly encountered in the occupancy area of the technical works (including possible disposal areas of excavated surplus or dredging materials). Special attention must be given in case of ecologically important (protected, endangered, rare or endemic) habitats, flora or fauna species being affected (e.g. the priority habitat “Posidonia beds - 1120”). Concerning the marine environment special emphasis should be given to priority habitats (according to annex I of the habitats Directive). As it is mentioned above, an AIAS has to be elaborated in case the marina is located into an area included into the European Ecological Network Natura 2000. 5) Socioeconomic environment: If the construction works take place into or close to residential or commercial areas socioeconomic negative impacts should also be expected. Additionally, any reference to the positive socioeconomic effects must be made.

Special attention must be given in cases where dredging material has to be disposed. The type of selected dredging method can reduce to a great extent the dispersal of marine pollution around

the dredging area (mechanical or hydraulic dredging, using of silt curtains) [6]. According to the Greek practice marine disposal of dredging material can take place in a depth greater than 50m and in a distance greater than 2Km of the coast. For the environmental approval of this type of disposal the environmental characterization of dredging material is needed. Although, there is no European legislation for the environmental characterization of dredging material, the European legislation related to waste characterization or other national methods (e.g. criteria used in Holland or U.S.A.) of environmental characterization of dredging material can be taken into account [6]. As for the European legislation, the Decision 2003/33/EC "Establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC" can be used. A clear picture not only of the type and the quantity of the contained pollutants in the dredging material, but of the potential they have to spread pollution is required. The evaluation of the existing environmental conditions of the possible disposal area(s) should be carried out.

Most of the impacts during construction are usually considered as short term and possible to mitigate. Permanent impacts are those which are related to the permanent occupancy of terrestrial and benthic ecosystems. Additional environmental impacts occur in case of using quarries or disposal areas.

The main categories of environmental impacts during the operation phase of marinas are mainly related to the following environmental means: 1) Geomorphology – Landscape: Construction of piers or wave breakers may cause significant impacts on the pre-existing status of marine sedimentation in the neighboring marine and coastal areas. Changes to the magnitude and/or direction of waves status near the coast, or sea water movement (due to wind activity or submarine currents) can lead to significant changes to sedimentation or erosion rates near the marina or/and along the coast. This phenomenon may also affect land uses and socioeconomic environment. In order to prevent such problems the planning phase of the marina can also include a coastal engineering study in which proper use of algorithms or simulation models can assess these impacts and also evaluate possible necessary modifications or adjustments on the design of the marina. 2) Marine ecosystems, fauna and flora species: One of the most challenging tasks is the preservation of high quality sea water inside and outside the marina. The design of the marina basin should ensure that proper circulation of seawater is not prevented and the mean concentration of dissolved oxygen remains high. The possible use of submarine openings on piers should be examined in case of enclosed marina basins. The use of impermeable septic tanks or waste water treatment facilities for municipal type waste water has also to be taken into account in case there is not neighboring available sewage network. During the operation phase high priority must be given to the prevention of sea pollution from all human activities that take place in the marina. This can be achieved by combining high quality environmental services provided by the staff and marina's facilities and the high environmental consciousness of marina's users. Emphasis should be given to the prevention of pollution from bilge water, lubricants, fuel, black and grey waters. Environmental friendly antifouling paints should also be used by the marina's users. If such measures are taken the impact on marine ecosystems may be reduced to a great degree. 3) Terrestrial ecosystems: Proper landscape restoration measures could mitigate possible impact on the terrestrial environment. 4) Land uses and traffic: for large scale marinas a proper assessment of the possible impacts on land uses and road traffic should take place in the EIAS. All accompanying uses of marinas should be taken into account (e.g. commercial activities) and on many occasions the elaboration of traffic models (for different scenarios) might be required. 5) Social and economic environment: The social and economic effects of marinas are positive, due to increase of tourism and employment. Marinas can also contribute to the promotion of the natural beauty, culture and history of the broad area, functioning as an intermediate between development, environment and society. In this respect, well designed and properly operated marinas can comprise the essence of sustainable development in coastal areas.

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All marinas should bear and have implemented a Regulation Framework for their Operation, as well as an Environmental Management Plan and a Contingency Plan (in case of emergency event). Additionally, an environmental monitoring programme is often proposed to be implemented in order to identify as early as possible abiotic or biotic trends that may result to environmental degradation. Marinas can also be certified by different environmental management schemes – standards, such as: ISO140001, EMAS (Eco-Management and Audit-Scheme), PERS (Port Environmental Review System), CLEAN MARINAS, GREEN MARINAS.

4. CASE STUDIES

4.1. Case Study A: EIAS of Leros Marina [7]

The Leros marina, with a capacity of 107 boats is located in the Greek island Leros. The marina includes an existing terrestrial area of 6.941m^2, a new terrestrial area of 29.571 m^2, a marine area of 52.860m^2 and an area for hauling up boats of 12.130m^2. The proposed works include a pier of total length of 330m, a dock of 12m width and 22m long, a ramp for boats of 29m length, six underground fuel tanks and a new service building. The Leros marina was environmentally approved in 2011. The possible environmental impacts of the project were assessed on most occasions as non significant with the exception of the estimated renewal capacity of the new marine basin. In order to prevent possible water quality problems, especially during periods of high phytoplankton concentrations a twin pipeline through the new pier for the renewal of sea water was proposed as a mitigation measure. Additionally proper stormwater drainage was foreseen in the terrestrial area, so that the marina basin remained free of rainwater and flashed pollutants.

4.2. Case study B: Environmental study for the modification of Environmental Terms of Limnos Marina [8]

The specific marina can accommodate 24 boats and is located in the Greek island of Limnos. The aim of the study was the modification of the designated Environmental Terms (Environmental Permit) due to technical modifications in the marina's design. The project included a marine area of 7.000m^2, a terrestrial area of 2.000m^2, changes in the shape and length of the windward (eastern) pier (from 90m to 108m), construction of a new west pier of 40m length and construction of a new administration building in an area of 153m^2. The differences between the environmentally approved and the final design of the project were determined, in order to estimate the differences in the environmental impacts. The environmental study for the modification of the Environmental Terms was approved in 2015. The differences between the environmentally approved and the new-final design were of small scale and consequently no significant differences were expected concerning possible environmental impacts. A specifically designed Environmental Management Plan was proposed. The latter included a monitoring programme focusing on the marine environment. The main parameters to be followed included turbidity, oils, phytoplankton, zooplankton, suspended particles, coliforms and dissolved oxygen and specific monitoring stations were proposed. The Environmental Plan included also specific measures for the protection of the manmade and natural environment and management of oil residues, used lubricants and toxic waste. A Contingency Plan was also proposed.

4.3. Case study C: EIAS for the developmental works of Poros harbor [9]

The aim of the study was the environmental permitting of the proposed development works of the existing marina and the planning of uses in Poros harbor. The proposed works optimize the spatial planning of uses in the harbor and included the following: the creation of an enlarged marina, which will be able to accommodate 178 boats, 115 in the north section and 63 in the south section, an administration building in the terrestrial section and a floating dock of 120m length in the marine

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section. Docking installations will be installed for the marina, which will include artificial boulders and bottom chains. The existing electromechanical equipment will be upgraded and the existing pavements will be replaced in the terrestrial area. Special attention has been given to the relation between the village of Poros and the marina, taking into account that the harbor is adjacent to the settlement of Poros, which has been declared as a Historical Monument, Site of Outstanding Natural Beauty as well as Traditional Settlement. During the construction phase of the project, possible impacts were identified and assessed on the morphology, the marine water quality (related to oil or lubricants leakage and runoff water from construction sites), the landscape (related to the presence of machinery and construction equipment), noise and air quality (related to work site functions). Appropriate mitigation measures were proposed for these impacts, including the implementation of best practice work site methods and techniques and the establishment of close cooperation between the local society and the constructor. A Contingency and an Environmental Management Plan (including monitoring) were also proposed.

4.4. Case study D: EIAS for a five stars Hotel and related marine works in Kea Island [10]

The aim of the project was the environmental approval of a Hotel, including a small harbor, covering a marine area of approximately 2.500m^2 and a terrestrial area of 75m^2. This harbor will accommodate diving services, as inflatable boats transporting divers will dock there and will be able to accommodate boats of 70m length or 4-5 yachts. The project was environmentally approved by the Greek State on 2012. Impacts on the sea environment were estimated taking into account the existing situation of the area of the proposed harbor. A specific study identifying the sea bio-communities was conducted, based on appropriate fieldworks. The following sea habitat types were identified and mapped: “1110 - Sandbanks which are slightly covered by sea water all the time”, “1170 - Reefs” and “1120 - Posidonia beds (*Posidonion oceanicae*)”. These habitat types are included in the Annex I of habitats Directive (92/43/EC), while habitat type 1120 is a priority habitat type. The area that will be occupied by the harbor is mostly reefs with photophile macroalgae and a small area of Posidonia beds (*Posidonia oceanica*). These areas constitute a very small percentage of similar habitats of the Vroskopos bay area and therefore the impacts were assessed as non significant, concerning the total coverage of habitat types and the functions of the ecosystem. The construction works planned included dredging and special attention was given to the investigation of possible disposal marine areas, which should meet the following requirements: distance of disposal area greater than 2Km from coast line, sea depth should exceed 50m outside of Posidonia beds, disposal should not form piles of more than 2m in height. Additionally, in order to further reduce the impact on posidonia beds, the external reinforcement of the harbor work was designed to be constructed with artificial boulders with steep inclination (4:3), so that the total footprint of the works remained as little as possible. Finally, for a period of two years after the completion of the project, any changes of the coastline will be closely monitored and a coastal engineering study will be conducted should any signs of possible impact are identified.

4.5. Case study E: EIAS for the development of the Hydra Port [11]

The proposed development of the existing port of Hydra island includes the following: the identification and management of existing and future port uses in order to provide services of high quality, including services to touristic boats. The port of Hydra will provide space for a total of 34 touristic boats (16 on the outer side and 18 vessels on the inner side of the windward pier). The aim of the study was the environmental permitting of the proposed development works of the existing port and the planning of uses. The proposed works will fully accommodate the existing uses, of the harbor and those that are expected in the future. The proposed uses and works within the port are: Creating docking for touristic boats, delimitation of land and marine area, strengthening the shield of windward pier and installation of vessel mooring system, bindings, waste and oil residues management with suitable collection reservoirs, maintenance and spatial organization of port uses

(passenger boats, fishing boats, etc.). During the construction phase greater impact is expected during strengthening the shield of the windward pier, the construction of mooring system and the disposal of some surplus materials. Local and short term increase in turbidity is expected to cause impacts on marine organisms. During operation phase no significant additional negative impacts are expected considering that the port is already in use and most of the port uses are already existed. A new Regulation of Port Operation and an Environmental Management Plan will be prepared by the Port Operator. A monitoring program and Contingency Plan are also proposed.

4.6. Case study F: Environmental study for the modification of the Environmental Terms for the development of the Port in New Epidaurus [12]

The proposed development includes expansion of the terrestrial area of the port, construction of a service building, strengthening and expansion of existing windward pier, replacing of the existing bridge, installation of mooring equipment, facility for fuel supply, etc. Impacts during construction are mostly related to the increase of sea turbidity due to works on the marine environment and the runoff of construction areas and materials. Possible pollution is expected mainly in case oil or lubricants leakage occurs. Priority shall be given to recycling especially for the shipwrecked boat that is now immersed in the port. The extension of the windward is proposed in order to include the unexploited coastal zone between the existing operating installations and the unexploited existing windward pier, while the proposed floating piers do not affect the existing natural movement of water. A new Regulation of Port Operation and an Environmental Management Plan will be prepared by the Port Operator. A monitoring program and Contingency Plan are also proposed.

4.7. Case Study G: EIAS for the Zea Marina [13]

Zea Marina is located on the east coast of the Piraeus peninsula. The marina area includes the internal port (Passalimani) and the external (Freatida). Due to dense residential and trade activities the urban area close to the marina is burdened by heavy traffic. The main task of the proposed project was the modernization of marina and the development of the terrestrial and marine zone in order to satisfy the existing needs and attract more touristic boats. The development plan of the marina creates the conditions for improving the efficiency of the Marina that can be achieved through increasing the capacity (to 580 vessels from 566), to the extent technically and legally possible, in an environmental friendly way which will primarily take into account the existing antiquities in the area. The project was environmentally approved in 2013. A special architectural study for protecting and giving prominence to underwater and terrestrial antiquities was carried out and was approved by the Central Archaelogical Council before the issuing of the Environmental Permit. Also a detailed traffic impact study was commissioned and attached to the EIAS study. The traffic study examined different senaria for the following 20 years and specific proposals were made for reducing possibel impacts on traffic conditions.

4.8. Case study H: EIAS for the Faliro Marina [14]

Faliro Marina is located on the south coast of the broad Athens metropolitan area. It is one of the most modern marinas in the Eastern Mediterranean since its construction was completed in 2004 for berthing luxury yachts in a pleasant, safe and luxurious environment. According to the EIAS small - scale additional port works are proposed in order to optimize existing marina's uses and ensure a proper cover of needs especially berths for larger yachts. These works include: Construction of new (west) guard pier as an extension of the existing anti-siltation construction, Remodeling of the crest and the inner side of the existing anti-siltation construction and construction of new platform, Reforming the existing western protection work of the internal basin, Dismantling the floating pier at northern front of the eastern pier of the internal basin and construction of new vertical front using bored piles, Remodeling of the superstructure of the internal basin by constructing outer front element, Repair windward pier, Removal of the two floating piers located in the inner basin and

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perform the necessary dredging works in the area of medium -sized yachts, Perform dredging in front of the western protective breakwater to ensure adequate depth for safe navigation to and from the marina. Direct impacts of small scale during the construction works were expected in the morphology of the sea bed and in particular in the areas where excavations and embankments are performed and in the designated area for the disposal of dredged materials. As the construction of the new harbor basin is near to the existing mouth of Kifissos river, and within the area where a tourist port already operates a sediments environmental characterization was carried out. The results showed that dredging material can be characterized in the category of non hazardous material, according to the Decision 2003/33/EC. According to the coastal engineering study, the comparative evaluation of simulation results concerning the current and future marine works, showed that the construction of the new works are expected to have a beneficial effect on coastal engineering behavior in Faliro marina. Turbidity problems are expected temporarily in the sea area where the dredged material will be disposed. An Environmental Management Plan and a Contingency Plan are proposed. Monitoring has also to include the regime of sedimentation on seabed near the marina.

5. CONCLUSIONS

Marinas are related to environmental impacts during the construction and operation phases. The significance of the impacts are related to the type and magnitude of marinas, the environmental sensitivity of the location area as well as the technical capabilities of mitigating environmental impacts. Environmental impacts can be reduced from the initial planning of the marina by selecting the most environmental friendly alternative solution. Examination of the sea sedimentation regime and circulation of sea water into the marina should also be examined. Impacts during construction can be mitigated to a great extend by using the best environmental friendly construction methods and materials. Mitigation of impacts during operation has to focus mainly on waste management and avoiding polluting the sea environment by marina's uses and the accompanying works and facilities. These should be achieved through the implementation and carrying out of the following: Regulation of Marina's Operation, Environmental Management Plan (including monitoring programme) and Contingency Plan. Staff training and environmental awareness of marina's users are also proposed. Given that the above mentioned are taken into account no significant impacts are expected for the natural environment and significant positive effects are expected for socioeconomic environment. This can contribute to the promotion of marinas sector as environmentally friendly infrastructures serving the human needs for recreation and experiential relation with natural environment.

References

[1] European Union, 2014. The EU explained: Environment, European Union, Directorate General for communication, Citizens information, 1049 Brussels, Belgium.

[2] The Superyacht, Summer 2001, Intelligence Quarterly Marina Capacity & Birth Analysis Report.

[3] University of Piraeus, 2012, Research for the Promotion of the importance of yachts on marine tourism and the national economy, Hellenic Chamber of Shipping.

[4] Marine Chamber of Greece, September 2013, National Strategy on Shipping Development.

[5] http://ec.europa.eu/environment/nature/natura2000/management/docs/art6/provision_of_art6_en.pdf (accessed March 1st, 2016).

[6] Papagrigoriou S.S., Bekiaris G.Y., 2010, Environmental management of Marine Aggregates in Greek harbour works, Fifth National Conference of marine works, National Technical University of Athens, Athens, 2010.

[7] ENVECO S.A., 2010. EIAS for the marina in the Temenia Area of Lakki bay in Leros.

[8] ENVECO S.A., 2014. Environmental study for the modification of the Environmental Terms of the marina in Limnos.

[9] ENVECO S.A., TRITON CONSULTING ENGINNERS, 2013. EIAS for the development works of Poros harbor.

[10] ENVECO S.A., 2011. EIAS for a five stars hotel in Kea island.

[11] ENVECO S.A., TRITON CONSULTING ENGINNERS, 2013. EIAS for the development works of Hydra port.
[12] ENVECO S.A., TRITON CONSULTING ENGINNERS, 2013. Environmental study for the modification of the Environmental Terms for the development of the Port in New Epidaurus.
[13] ENVECO S.A., 2008. EIAS for the Zea Marina.
[14] ENVECO S.A., TRITON CONSULTING ENGINNERS, 2012. EIAS for the Faliro Marina.

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Geospatial assessment of the pollutant load trend in a coastal marine area

F. Sakellariadou

Department of Maritime Studies, University of Piraeus, 18532 Piraeus, Greece.
Email: fsakelar@webmail.unipi.gr

Abstract

Coastal areas are fragile and sensitive zones supporting a wide range of habitats and ecosystems. They are regarded as the most productive areas while they show a high attraction for human settlement. Consequently, coastal areas show a high potential for strong environmental pressure that may lead to biodiversity loss, habitat destruction and elevated pollution loads. Therefore, it is essential to quantify the environmentally significant pollutants, identify and classify their sources and find out their diffusion pattern. A useful aid for this study is the application of a geostatistic approach that furnishes prediction surfaces for the pollutant content. This procedure allows a significant monitoring of the area and it also specifies the sites of a particular concern. Furthermore, it supports the concept of Integrated Coastal Zone Management providing comments for the application of coastal spatial planning.

In the present paper this procedure is applied in a specific coastal marine area, the geospatial pollutant distribution is studied and conclusions are drawn for their transport and the respective environmental pressure.

Keywords: coastal zone; diffusion trend; geostatistic; metal; pollution

1. INTRODUCTION

Coastal zones are characterised by a high environmental, economic, social, cultural and recreational importance recognised by their exceptional biodiversity in terms of flora and fauna. They are the most productive areas in the world providing a wide variety of habitats and ecosystem services while they offer a unique environment. Coastal zones are regarded as sensitive and fragile areas and local communities have to face a wide range of environmental conditions. They are regarded as a major carbon sink and a substantial oxygen source playing a vital role in regulating the climate as well as the global ecosystem. Furthermore, during the long history of human being, there was always a close relationship between humanity and coasts. The major part of the total transportation, trade, infrastructure, rural and agricultural development, energy processing, tourism and recreation corresponds to the coastal zone [1]. Consequently, coastal zones suffer by excessive exploitation and environmental pressure. Nowadays, coastal ecosystems have to face the threat of biodiversity loss, habitats destruction, pollution, conflicts between potential uses and space congestion problems. Coastal areas could be seriously affected by climate change and more specifically by sea level rise, changes in the intensity and frequency of storms, increases in precipitation, higher ocean temperature and ocean acidification caused by the increase of the atmospheric content in carbon dioxide. Climate change impacts are likely to worsen many difficulties that coastal areas already face.

It is obvious that there is a need of specific strategies ensuring the conservation of the environment and allowing the sustainable use of the area. The well being of local coastal populations and the economic viability of respective business uses depend on the environmental

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health, the protection of coastal resources and the increase of the efficiency of their uses. This is achieved by applying Integrated Coastal Zone Management, ICZM, which integrates economic, environmental and social issues, balancing their objectives within a specific framework set by natural dynamics with reference to the ferrying capacity of the ecosystem. IZCM respects natural resources and promotes environment's and ecosystems' health, the so-called "ecosystem based approach" offering a substantial contribution to the sustainable development of coastal zones. This procedure includes a range of stages such as information collection, planning, decision-making, management and monitoring of implementation.

1.1 Coastal marine area

The coastal marine area is part of the coastal zone which is the zone of Earth where terrestrial environments influence marine ones and the vice versa. Coastal marine area is the part of the sea directly affected from the land as result to their proximity. According to the Protocol on Integrated Coastal Zone Management in the Mediterranean, signed at the Conference of the Plenipotentiaries [2] the interaction between the marine and land parts of the coastal zone arises as complex ecological and resource systems made up of biotic and abiotic constituents coexisting and interacting with human communities and appropriate socio-economic activities

1.2 Sea bed sediments

Pollutants accumulated in the water column are likely to be scavenged by particulate matter and co-precipitate at the sediment floor being finally deposited to the sediment matrix. Therefore, sea sediments are considered as physical traps for many environmental pollutants acting as important reservoir for contaminants [3, 4]. This mechanism can build up to chronic pollution levels resulting in ecological degradation with potential severe impacts on marine bio-communities' and species' well-being; the possibility of cascading effects upon human health through the food web as well as effects upon the economy. As sea sediments act like archives of environmental pollution trends, dated sediment cores measurements reveal the effectiveness of convention and regulations to control and eliminate the environmental input of pollutant loads.

The distribution of contaminants in marine sediments is related to factors such as the spatial and temporal variability of inputs, the various transport mechanisms, the chemical speciation, the contaminant mobility, the redox conditions, the sediment grain size, etc.

1.3 Pollution dispersion

Coastal areas suffer by a wide variety of pollutants. In order to eliminate and handle their risky impacts it is essential to assess pollutant concentrations, identify and classify their sources and discover their diffusion pattern. It is obvious that there is an absolute need to transform data into more useful products that allow the identification of possible patterns and relationships. This can be achieved through GIS that has this capability. The construction of spatial distribution patterns for sediment contaminants allows remarks about the pollution trend [5, 6].

The pollutants studied in the current study are environmentally significant heavy metals. They have high toxic properties and harsh effects on the abiotic and biotic systems. They are accumulated in reservoirs by biological and geochemical mechanisms causing severe problems.

2. MATERIALS AND METHODS

Thirty surface sediment samples were collected from the Elefsis gulf using a Van Veen grab. The gulf is named after the city lying on its coasts, at 20km distance westwards of Athens. It is mainly surrounded by Attiki peninsula except of its southern part where the island of Salamina lies. Two narrow entrances allow the water's circulation with the "open" sea. Along its northern coasts there

are various heavy industry units. There are also two harbours and two spots with liquid fuel tank. The gulf acts too as a main passage for tankers, cargo ships and ferry boats.

All sediment samples were treated by hand for the removal of unrepresentative material and then homogenized. Samples were dried at 40°C and thoroughly ground using a small pestle and mortar. They were digested with a mixture of concentrated acids (HNO_3-HF-$HClO_4$) in screw capped Teflon beakers on a hot plate [7] for the determination of the total metal content. Metal concentrations were measured with Flame Atomic Absorption Spectrophotometry (Varian Spectra AA-200 model equipped with deuterium lamp for background correction) and Graphite Furnace Atomic Absorption Spectrophotometry (AAS), (Varian Spectra AA-640Z GTA 100 model, equipped with Zeeman). The sediment reference used was IAEA433. In a following step a geodatabase was created by applying the ArcGIS software [8].

2.1 Sampling design

Sampling design was based on parameters including the appropriate number of samples in relation to area size, the anthropogenic activities, the pollutant pathways and possible distributions, the sediment and organic matter characteristics, the seabed bathymetry and prevailing currents as well as the statistical resolution needed.

2.2 Interpolation methods

The generation of a pollution dispersion surface needs data interpolation by which a limited number of sample points are used to predict the values for new points in order to generate a surface. Two interpolation methods are generally used within spatial analysis techniques. These are called deterministic and geostatistical interpolation. Deterministic interpolation assigns values to locations based on the surrounding measured values within an area around the point to be interpolated and a weighted average of the values is then calculated. As distance from the point increases, the weightings decrease to reflect error/variance. IDW is one of the most frequently used deterministic models in spatial interpolation. This is because it is relatively fast and easy to interpret. It generates surfaces using the assumption that the value of an unsampled point is the weighted average of known values within a specified neighbourhood. The weights are inversely related to the distances between the prediction location and the sampled location [9]. Geostatistical methods are based on statistical models that include autocorrelation as well as weighted distance calculations. As a result, geostatistical techniques can produce a prediction surface as well as provide some measure of the certainty or accuracy of the predictions. The Kriging approach [9, 10, 11, 12] refers to a geostatistical method of interpolation providing values at un-sampled locations taking into consideration the original data set of the regionalised variables as well as the structural features of the variogram. Kriging analyses the spatial structure of the data, integrates the averaged spatial variability of the data and allows for a measure of the accuracy of the predictions. The variogram (or semi-variogram) is a graph relating the variance of the difference in value of a variable at pairs of sample points to the separation distance between those pairs. This relationship can in addition be calculated for different directions [13]. According to the Simple Kriging interpolation technique, a generalised linear regression is applied while either semivariograms or covariances (which are the mathematical forms used to express autocorrelation) are employed.

3. RESULTS AND DISCUSSION

Interpolated metal concentrations are illustrated in Figures 1 - 10. They show very clearly the diffusion pattern of the pollutants as well as their main sources. The heavy industrial units situated on the northern coastal area affect seriously the dispersion of heavy metals such as Cr, Mn, Fe, Cu, Zn, Cd and definitely Pb.

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The lower metal enrichment at the western part of the gulf could be attributed to the corresponding reduction in intensive pollution sources though there are fuel tanks nearby. It should be noticed that the geological features of the gulf are characterised by a variety of soil composition as well as the presence of subsea currents contributing to material transport and sediment mobilisation. The above mentioned lower metal content at the western exit of the Elefsis Bay could also be partially attributed to the grain size of the material covering the seabed, which is characterised as coarse sand [14], potentially reflecting the shallower depth at these sites. Notably contaminant material has a greater affinity for fine sediment and organic matter.

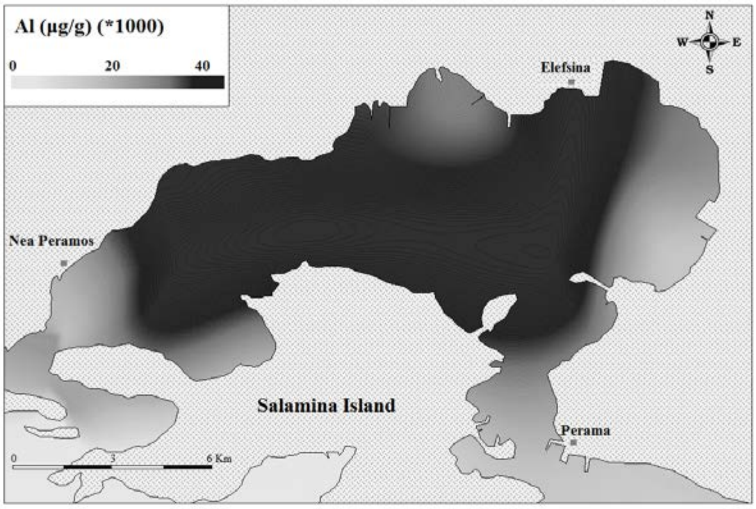


Figure 1. Prediction surface for Al content in sediment samples.

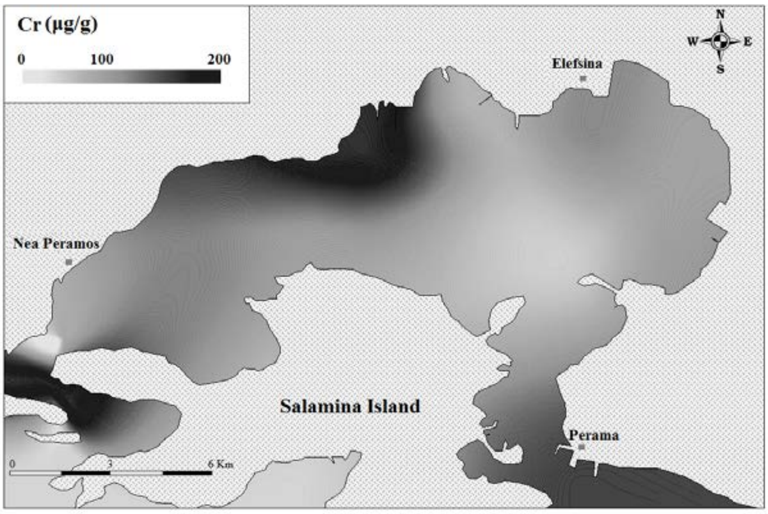


Figure 2. Prediction surface for Cr content in sediment samples.

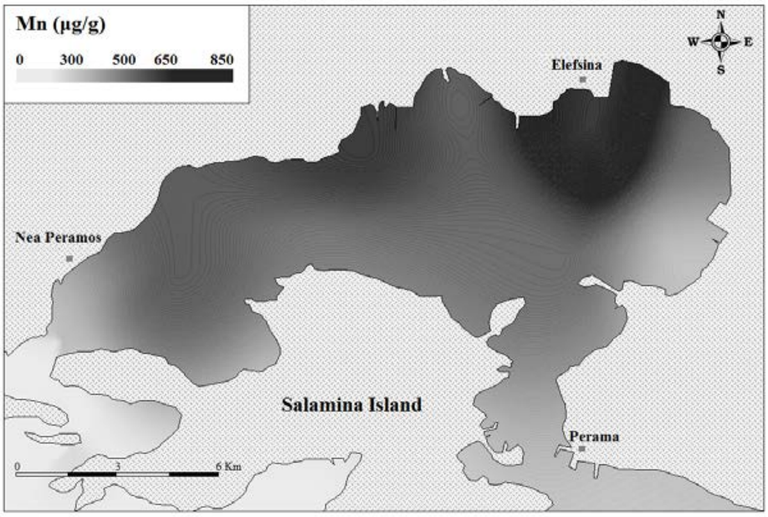


Figure 3. Prediction surface for Mn content in sediment samples.

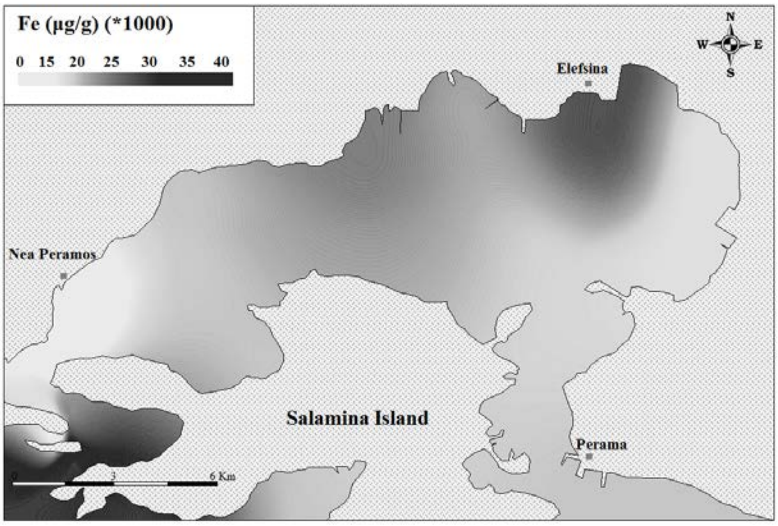


Figure 4. Prediction surface for Fe content in sediment samples.

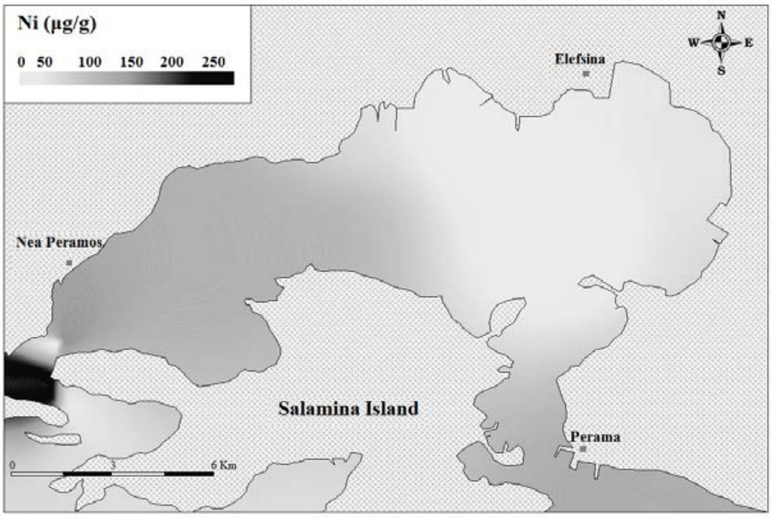


Figure 5. Prediction surface for Ni content in sediment samples.

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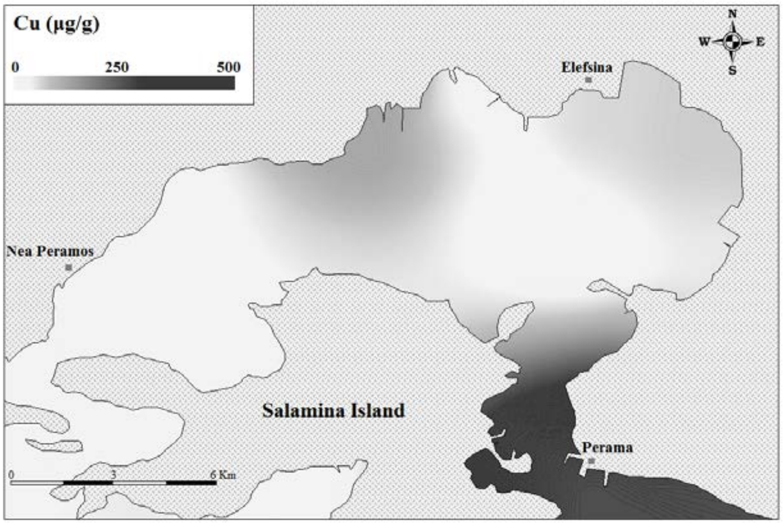


Figure 6. Prediction surface for Cu content in sediment samples.

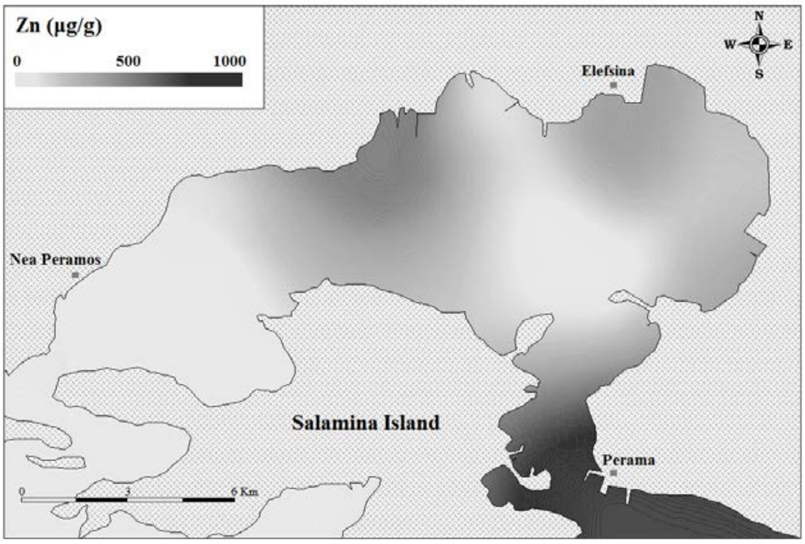


Figure 7. Prediction surface for Zn content in sediment samples.

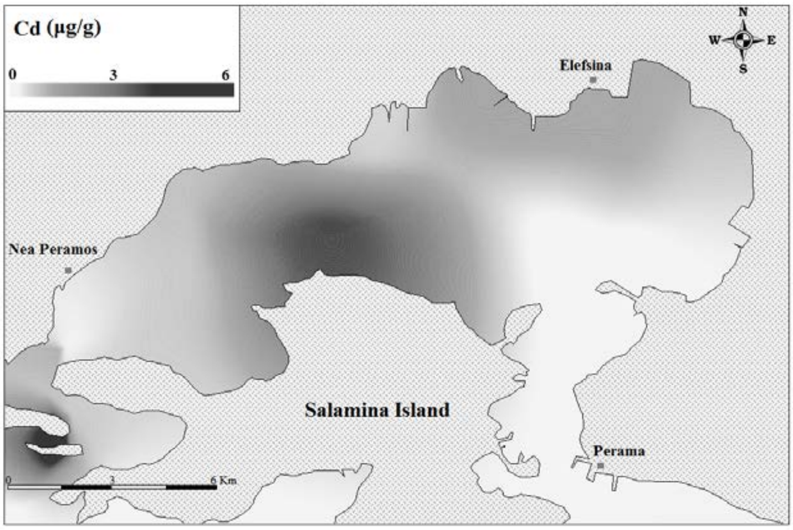


Figure 8. Prediction surface for Cd content in sediment samples.

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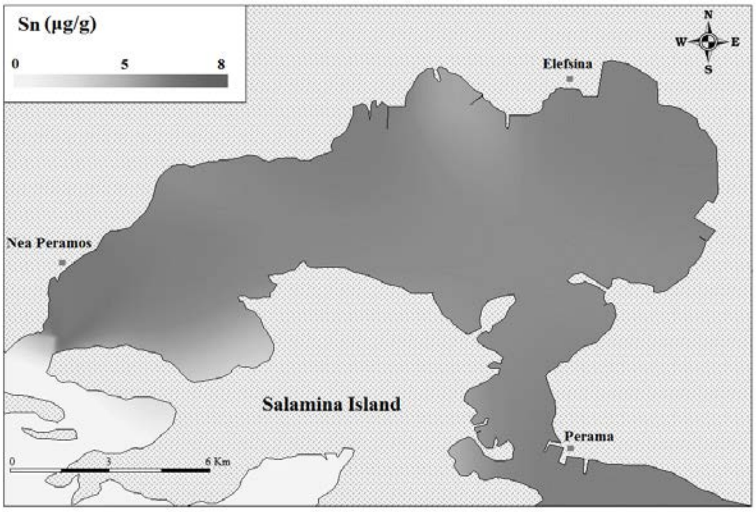


Figure 9. Prediction surface for Sn content in sediment samples.

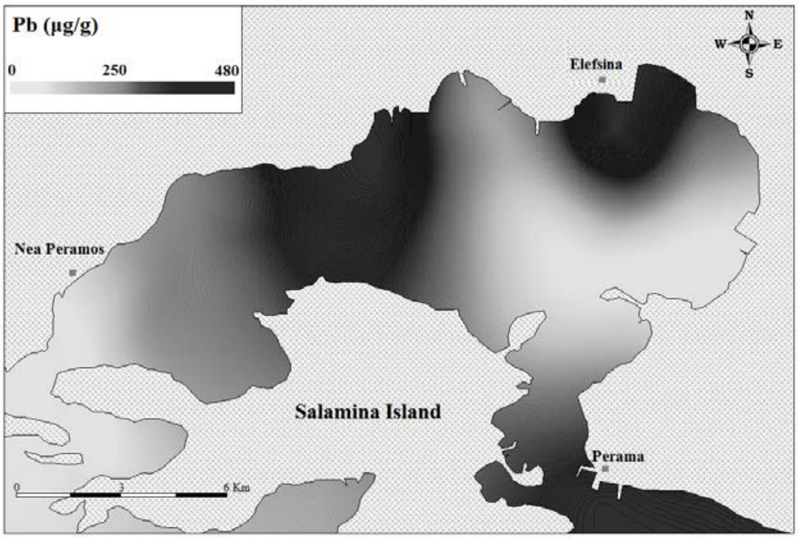


Figure 10. Prediction surface for Pb content in sediment samples.

4. CONCLUSIONS

The status and trend of marine chemical pollution serve the needs of an environmental monitoring procedure while offers a tremendous help towards an effective environmental awareness-raising effort. The pollutant dispersion trend is essential in order to keep the environmental pressure below the ferrying capacity of the ecosystem, allow a better land use pattern and identify the major pollutant sources. This trend can be found out by using the appropriate geostatistic approach providing with multiple geospatial maps. This approach satisfies also the requirements of coastal and marine spatial planning.

In the current study the Simple Kriging interpolation technique was applied in an effort to reveal the pollutant spatial distribution in the gulf of Elefsis that is well known for its industrialised northern coastal area.

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References

[1] Sakellariadou 2014.The concept of marine ecotourism: Case study in a Mediterranean island. *The International Journal of Climate Change: Impacts and Responses*, **5**. http://www.on-climate.com (accessed March, 2, 2014).

[2] The Protocol on Integrated Coastal Zone Management in the Mediterranean, signed at the Conference of the Plenipotentiaries, Madrid, January 21, 2008. http://www.pap-thecoastcentre.org/razno/PROTOCOL%20ENG%20IN%20FINAL%20FORMAT. Pdf (accessed December 20, 2015).

[3] Salomons W. and Förstner U., 1984. *Metals in the Hydrocycle*. Springer Verlag.

[4] Burton G.A. Jr., 2002. Sediment quality criteria in use around the world. *Limnology*, **3**, 65-75.

[5] Steyl I., Sakellariadou F. & Bray S., 2013. *Quantification of Pollution levels in harbour Sediments –a GeoSpatial Perspective*, Tahoka Press.

[6] Sakellariadou, F., 2013. The use of multivariate and geostatistical analysis for the evaluation of quality of coastal marine environment. *Proceedings of CIESM*, 28 October – 1 November, Marseille, France.

[7] UNEP, 1985. *Reference Methods for Marine Pollution Studies*, No 31-39.

[8] ESRI (Environmental Systems Research Institute), 2012. ArcExplorer Desktop. http://www.esri.com/software/arcgis/explorer (accessed December 6, 2015).

[9] Lu, G.Y. and Wong, D.W., 2008. An adaptive inverse – distance weighting spatial interpolation technique. *Computers & Geosciences*, **34**, 1044 – 1055.

[10] Longley, P.A., Goodchild, M.F., Maquire, D.J and Rhind, D.W., 2001. *Geographic Information Systems and Science*. John Wiley & Sons, Ltd., Chichester.

[11] Yunfeng, X., Chen, T., Lei, M., Yang, J., Guo, Q., Song, B and Zhou, X., 2011. Spatial distribution of soil heavy metal pollution estimated by different interpolation methods. Accuracy and uncertainty analysis. *Chemosphere*, **82**, 468 – 476.

[12] Gu, Y.; Wang, Z.; Lu, S.; Jiang, S.; Mu, D & Shu, Y., 2012. Multivariate statistical and GIS – based approach to identify source of anthropogenic impacts on metallic elements in sediments from the mid Guangdong coasts, China. *Environmental Pollution*, **163**, 248 – 255.

[13] Chrisman, C., 1997. *Exploring Geographic Information Systems*. John Wiley & Sons, New York.

[14] Scoullos, M.J., 1986. Lead in coastal sediments. The case of the Elefsis Gulf, Greece. *The Science of the Total Environment*, 49, 199 – 219.

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Renewable and Sustainable Energy Management and Planning

PROTECTION
AND
RESTORATION
OF THE
ENVIRONMENT
XIII

Determining optimal siting areas for wind farms in the regional Unit of Chania, Crete in Greece

E. Emmanouilidi*, D. G. Vagiona

School of Spatial Planning and Development, Faculty of Engineering,
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
*Corresponding author: Email: vemmman90@gmail.com

Abstract

The goal of the European energy policy about the development of "clean" energy, combined with the rapidly increasing energy demand, has led to the enhancement of the interest in exploitation of Renewable Energy Sources (RES), which are extremely ecological friendly forms of energy. The utilization of RES in Greece and wind farms in particular, is the number-one challenge in the field of energy. The phenomenon of uncontrolled wind facilities siting, causes land use conflicts, social reactions and proves the weakness of a comprehensive, prudent use of natural resources, resulting in inadequate protection of the natural and human environment. The present paper deals with the issue of the determination of Optimal Siting Areas (OSA) for wind farms, particularly in the Regional Unit (RU) of Chania, Crete in Greece, in the framework of Geographical Information System (GIS) by implementing the Analytic Hierarchy Process (AHP).

Keywords: Renewable Energy Sources (RES); wind farm siting; Analytic Hierarchy Process (AHP); Geographic Information Systems (GIS); Chania

1. INTRODUCTION

The increased living standards of modern society, the continuous population growth, combined with global warming and climate change are notable factors, which create strong interest to promote alternative and greener energy sources. Renewable Energy Sources (RES) are environmental friendly energy sources since by their usage, environmental impacts and energy losses are reduced and significant fuel saving is achieved. Thus, RES constitute an essential component of sustainable development and must be taken into consideration in future energy production plans.

Regarding the rate of participation in power production, wind farms stand out as RES technologies. However, the wind farm siting is an essential issue, since their mass construction at the beginning of their growth, without any legislative guidelines, has led to uncontrolled siting, creating many social and environmental effects. An integrated policy for wind farm siting issues, satisfying the need for rational planning and programming on this specific field, was introduced by the Greek legislative framework (Special Framework for Spatial Planning and Sustainable Development for Renewable Energy Resources – SFSPSD) [1] at 2008.

The siting process of RES facilities consists of a number of parameters described, both in environmental as well as social-economical and technical data. The multitude of factors involved in the siting process necessitates the use of computer systems. Geographic Information Systems (GIS) are flexible spatial data management and performance tools. This type of software offers the possibility to create dynamic maps and to integrate both existing data and any future amendments. GIS are essential for the implementation of spatial analysis methods, since the spatial resolution is determined by the management of spatial data, which are organized in them. Numerous studies have

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been found in the literature involving the use of GIS, in order to apply wind farm location criteria [2, 3, 4, 5, 6, 7]. Baban and Parry (2001) [8], for instance, applied a GIS (IDRISI) in order to apply wind farm location criteria using two different methods to combine information layers for a site in Lancashire (UK).

Along with Geographic Information Systems various methodologies such as multi-criteria analysis (MCA) have been developed and implemented, for solving similar siting problems, to integrate, apart from purely technical aspects, the environmental and social-economical factors. MCA also referred as multi-criteria evaluation (MCE) methods allow analysis of complex, multi-dimensional trade-offs between choice alternatives for example locations or suitability analysis of an area [9, 10]. One of the multi-criteria decision making (MCDM) models is the Analytic Hierarchy Process (AHP) that was first appeared in 1980 by Saaty [11]. According to this method, the original problem is divided into individual segments or variables, which are classified hierarchically, giving numerical values to the estimates of the relative importance. Finally, the assessments' combination, determines which variable has the highest priority/influence on the result. Essentially, this method provides the ability to review, prioritize and parse many conflicting environmental and social-economical criteria. This specific model of MCDM has been applied in several studies. Effat (2014), Tegou et al (2010) and Bennui et al (2007) have applied the Analytic Hierarchy Process in order to define the relative weights to the criteria by making binary comparisons of them, for the determination of the most suitable sites for wind farm development projects.

The aim of this paper is to develop a methodology of an integrated assessment and hierarchy of selected areas, to determine the Optimal Siting Areas (OSA) for wind facilities, in Regional Unity (RU) of Chania, Crete in Greece. The rest of the paper is organized as follows: section 2 provides insightful descriptive details into the area of interest, and section 3 presents the methodology performed as well as the selected exclusion and evaluation criteria. Section 4 presents the optimal areas for wind farm siting and their contribution to the energy production of the study area, whilst section 5 provides concluding remarks together with some policy implications.

2. STUDY AREA

The Regional Unit of Chania is located in the westernmost quarter of the Crete island. Its total area is 2,376km^2, with 171.822 inhabitants, according to the National Census of 2011, and a population density equal to 66 inhabitants/km^2. According to the Regulatory Authority of Energy (RAE) [12], Crete belongs in the non-interconnected islands system i.e. the Greek islands whose electricity distribution network is not connected to the mainland distribution system. The share of RES in electricity production in Crete in December 2014 is 18.04%. Regarding the energy production from RES and especially from wind and solar energy, the figures given by the Hellenic Electricity Distribution Network Operator (HEDNO), for the December of 2014, show that wind farms (W/F) produce far more energy than the photovoltaic systems (P/S). Regarding to the RU of Chania, a 9,5% decrease of the produced wind farms energy is observed during the period of 2012-2014.

3. METHODOLOGY

The methodology used to select the optimal siting area (OSA) for wind farms in RU of Chania, includes certain stages (Figure 1) that are analyzed below. This separation process enables the researcher to carry out potential reviews and corrections that may be needed at any stage.

First of all, the exclusion stage is performed, in which the exclusion criteria/areas, minimum distances that need to be kept from exclusion areas and some additional restrictions are defined, in order to make the remaining available areas exploitable for the installation of a wind power plant.

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Thereafter, the evaluation criteria are selected, according to which every available area chosen for evaluation, will be further investigated.

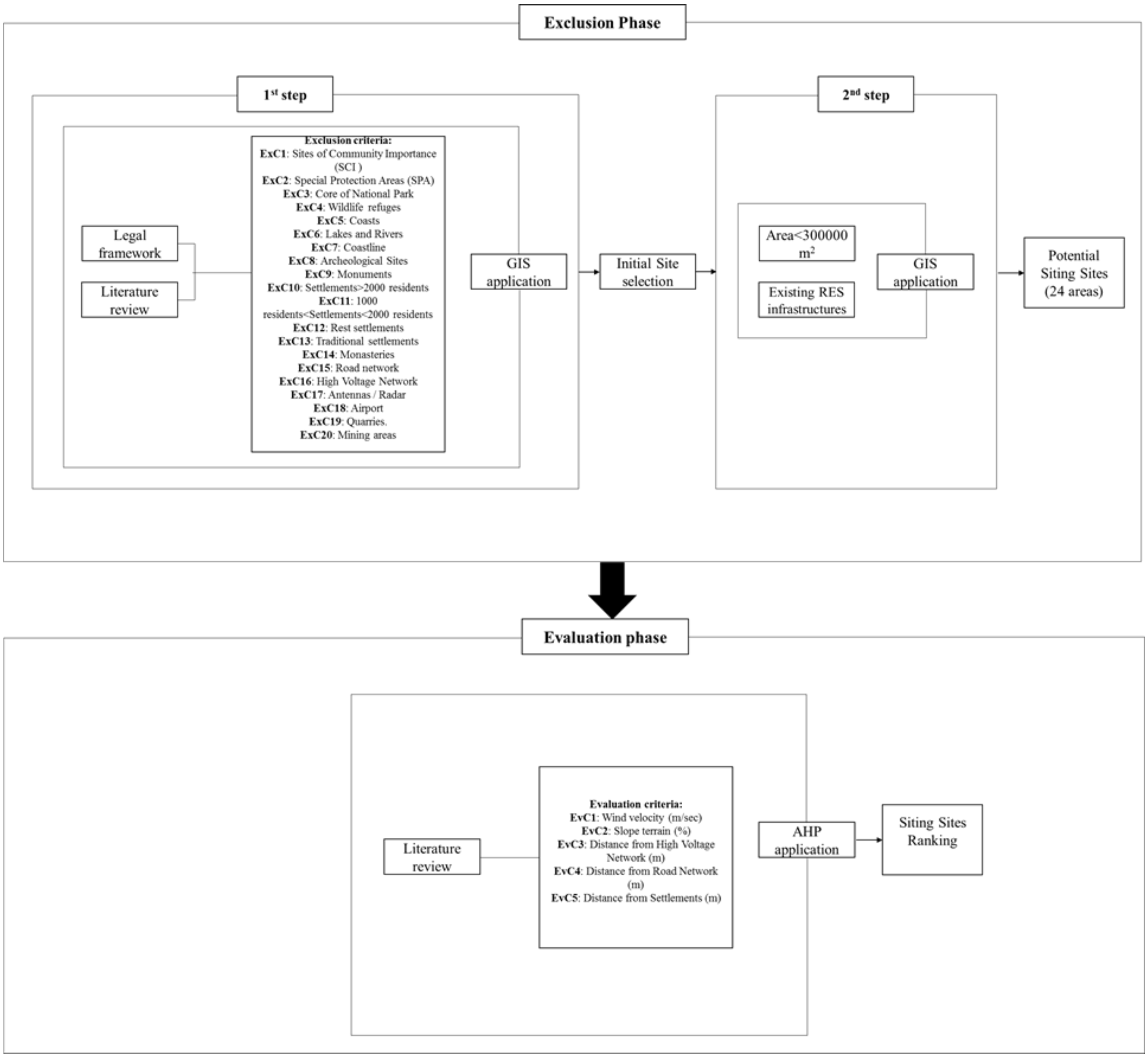


Figure 1. Methodological approach

3.1 Exclusion Stage

At the initial stage exclusion/incompatible areas are specified. Specifically, the exclusion criteria and minimum distances selection is performed, according both to the National Institutional Framework concerning the wind farm siting issues [1], as well as to corresponding examples of wind farm siting found in the literature [2, 3, 4, 5, 6, 7, 8, 13, 14].

3.1.1 Exclusion criteria

Exclusion areas include point, linear and polygon exceptions, as shown in Table 1. It should be mentioned that lakes, rivers and wildlife refuges are not included in the exclusion areas mentioned in the SFSPSD. The reason that the first two areas are excluded is clearly obvious, since onshore wind farms cannot be developed on rivers and lakes. Wildlife refuges are selected as exclusion areas, due to the sensitive wildlife flora and fauna that can be disrupted by the construction and operation of the wind farm facilities.

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3.1.2 Minimum distances

The depiction and presentation structure of the following categories is based on the Annex II of the Renewable Energy Special Framework that analyzes the minimum distances that must be kept from neighboring land uses, activities and technical infrastructure networks. The final minimum distances (Table 1) are specified by the combination of the above Special Framework's guidance and the distances found and compared in the wind farm siting literature [2, 3, 4, 5, 6, 7, 8,13,14].

Table 4. Exclusion Criteria and Minimum Distances

	Exclusion Criteria	Type	Minimum Distances
ExC 1	Sites of Community Importance (SCI)	Polygon	1000m
ExC 2	Special Protection Zones (SPA)	Polygon	1000m
ExC 3	Core of National Park	Polygon	1000m
ExC 4	Wildlife Refuges	Polygon	1000m
ExC 5	Coasts	Point	1500m
ExC 6	Lakes/Rivers	Polygon/Linear	300m
ExC 7	Coastline	Linear	2000m
ExC 8	Archeological Sites	Linear	1000m
ExC 9	Monuments	Point	700m
ExC 10	Settlements>2000res.	Polygon	1500m
ExC 11	1000res.<Settlements<2000res.	Polygon	1000m
ExC 12	Rest Settlements	Polygon	500m
ExC 13	Traditional Settlements	Polygon	2000m
ExC 14	Monasteries	Point	500m
ExC 15	Road Network	Linear	150m
ExC 16	High Voltage Network	Linear	150m
ExC 17	Antennas/Radars	Point	120m
ExC 18	Airport	Point	3000m
ExC 19	Quarries	Polygon	500m
ExC 20	Mining Areas	Polygon	500m

3.1.3 Further restrictions

At this point, a further analysis is performed to find out whether the areas from the previous stage can be considered available. Using such an automated process (GIS, ArcMap) in order to edit and enhance the suitable areas, the areas that arise are essentially filtered only by the mathematical procedures of a computer. Therefore, although some areas may be considered appropriate for the chosen criteria, they probably cannot be used due to some further restrictions.

The size of each area is one of those restrictions. It is considered appropriate to remove from the available sites, those with surface less than 300.000m^2, i.e. 0.3km^2, due to the adequacy of large areas that emerged and the inability to install wind farm facilities in such small areas (polygons). Moreover, another feature that should be considered is the existing power plants, some of which coincide with areas emerged. Finally, the criterion of the 0.3km^2 areas is further applied in areas emerged after the deduction of land with existing RES facilities.

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Table 5. Phases of Exclusion Stage

1st Phase: Exclusion Criteria & Minimum Distances		
	Area (km^2)	**Coverage area of the RU**
Initial areas	190.5	8%
Excluded areas	2156	91%
2nd Phase: Further restrictions		
	Area (km^2)	**Coverage area of the RU**
Available areas	148	6%
Excluded areas	2200	94%

3.2 Evaluation Stage

Twenty four polygons-regions are selected, mainly by their area and the wind potential. These regions are further evaluated, in order to find the optimal siting area for wind farms.

To determine the evaluation criteria, great importance is attributed to the economic efficiency of the potential wind farms, since the necessary environmental protection is ensured at the previous stage where the unsuitable areas are excluded. The appropriateness of the selected alternative areas is investigated not only in terms of economic efficiency, but also in terms of the minimum cost installation. The criteria examined in this stage are described in Table 3.

Table 6. Evaluation Criteria

Evaluation Criteria		Abbreviation	Policy Relevance	Limit	Type
EvC1	Wind Speed (m/s)	WS	Technical/Economic	≥4m/s	Benefit
EvC2	Slope Terrain (%)	ST	Technical/Economic	<25%	Cost
EvC3	Distance from HV Network (m)	DHVN	Economic		Cost
EvC4	Distance from Road Network (m)	DRN	Economic		Cost
EvC5	Distance from Settlements (m)	DS	Environmental/Social		Benefit

For the determination of the optimal wind farm siting area, the Analytic Hierarchy Process, which was developed by Saaty (1980) is performed. It is a process of converting subjective scores with relative weight in a set of scores or gravities used in problems with discrete choices. It addresses the problem of gravity (weight) distribution in a set of activities, according to their level of relevance.

During the comparison process, the data of each hierarchy level are compared with the other element of the same level, using as criteria the elements of the upper level (Figure 2) and the comparison starts at the 1st level.

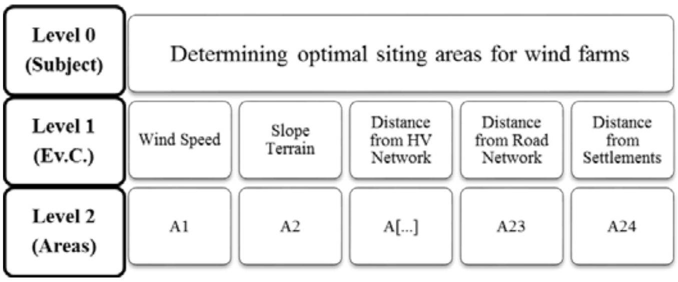


Figure 2. AHP levels

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4. RESULTS

The available areas resulting from the exclusion stage, are depicted in Fig. 3. The circled polygons represent the alternative sites selected for evaluation based on their extent and wind potential for the determination of optimal siting areas suitable for both installation and operation of wind farm facilities.

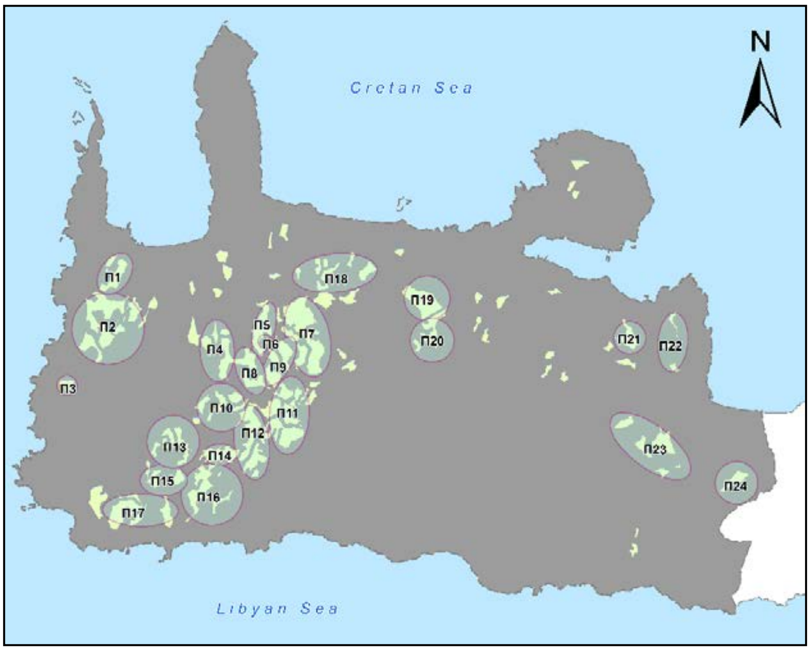
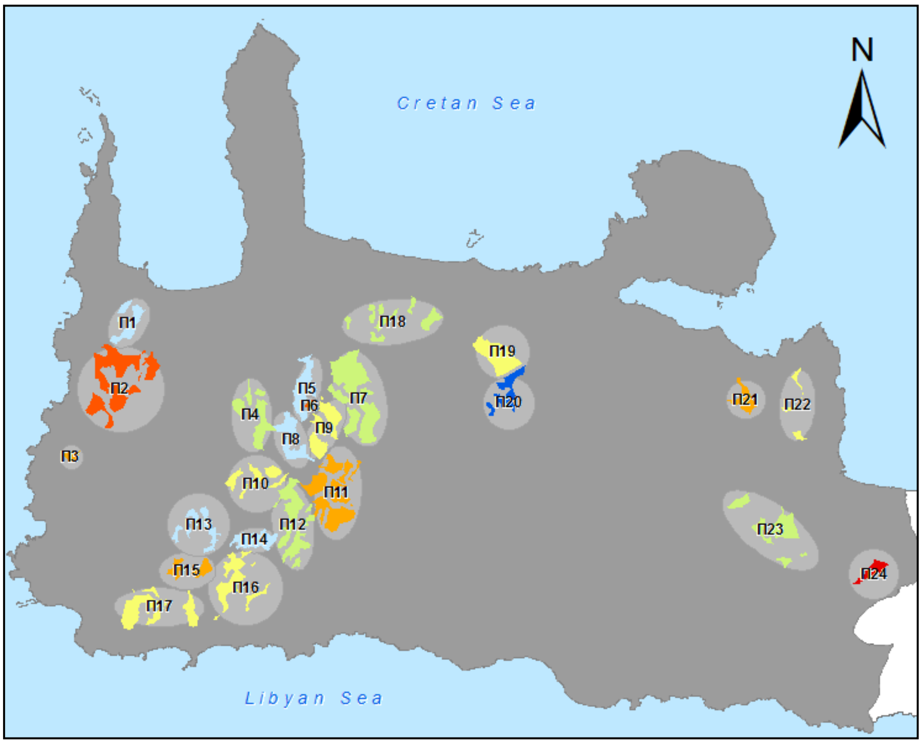


Figure 3. Available Areas/Evaluation Areas



Extremely High
High
Relatively High
Neutral
Relatively Low
Low
Extremely Low

Figure 4. Evaluation Areas' Priorities

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Figure 4 presents the appropriate areas based on their priority in the optimal siting issue of wind farm facilities in accordance with the selected criteria and the Analytic Hierarchy Process. Thus the different color of each area represents the level of suitability for wind farm siting (extremely high: blue to extremely low: red).

5. CONCLUSIONS

The aim of this research is to develop a methodology in order to determine the Optimal Siting Areas (OSA) for wind farm development projects, in Regional Unity (RU) of Chania, in Greece. This specific methodology is based both on the existing (2015) legal framework, and the Greek and foreign literature review regarding wind facilities siting. The tools used in the analysis are the Geographic Information System, specifically the ArcMap 10.2.2 and the Analytic Hierarchy Process.

The aforementioned methodology is simple and objective. Moreover, it contributes to sustainable energy development in line with current legislation. An integration of economic, technical, environmental and social consequences of wind farm siting has been taken into consideration. The Optimal Siting Areas are assessed in order to affect to the less possible extend the natural and the human environment as well as the return of the investment in this sector. Therefore, the configuration of a vision with reference to sustainable energy production systems, based on available resources and characteristics of each region is promoted. The alignment of energy and environmental policies is, at the same time, facilitated towards sustainability.

References

[1] Special Framework for Spatial Planning and Sustainable Development for Renewable Energy Resources – SFSPSD, 2008.

[2] Latinopoulos D., Kechagia K., 2015. A GIS-based multi-criteria evaluation for wind farm site selection. A regional scale application in Greece. *Renewable Energy*, **78**, 550-560.

[3] Effat H., 2014. Spatial Modeling of Optimun Zones for Wind Farms Using Remote Sensing and Geographic Information System, Application in the Red Sea, Egypt. *Journal of Geographic Information System*, **6**, 358-374.

[4] Haaren R., Fthenakis V., 2011. GIS-based wind farm site selection using spatial multi-criteria analysis (SMCA): Evaluating the case for New York State. *Renewable and Sustainable Energy Reviews*, **15**, 3332– 3340.

[5] Tegou L.I., Polatidis H., Haralambopoulos D.A., 2010. Environmental management framework for wind farm siting: Methodology and case study. *Journal of Environmental Management*, **91**, 2134-2147.

[6] Aydin N.Y., Kentel E., Duzgun S. (2010). GIS-based environmental assessment of wind energy systems for spatial planning: A case study from Western Turkey. *Renewable and Sustainable Energy Reviews*, **14**, 364–373.

[7] Bennui A., Rattanamanee P., Puetpaiboon U., Phukpattaranont P., Chetpattananoddh K., 2007. Site Selection for Large Wind Turbine Using GIS. *PSU-UNS International Conference on Engineering and Environment - ICEE-2007*, Phuket May 10-11, 561-566.

[8] Baban S.M.J., Parry T., 2001. Developing and applying a GIS-assisted approach to locating wind farms in the UK, *Renewable Energy*, **24**, 59–71.

[9] Szurek M., Blachowski J., Nowacka A., 2014. Gis-based method for wind farm location multi-criteria analysis. *Mining Science*, **21**, 65−81.

[10] Meng Y., Malczewski J., Boroushaki S., 2011. GIS-Based Multicriteria Decision Analysis Approach for Mapping Accessibility Patterns of Housing Development Sites: A Case Study in Canmore, Alberta. *Journal of Geographic Information System*, **3**, 50-61.

[11] Saaty T.L., 1980. The Analytic Hierarchy Process. New York, McGraw-Hill.

[12] Regulatory Authority of Energy (RAE). http://www.rae.gr/site/en_US/portal.csp. Last visit: 16/4/2016

[13] Voivontas D., Assimacopoulos D., Mourelatos A., 1998. Evaluation of Renewable Energy Potential Using A GIS Decision Support System. *Renewable Energy*, **13(3)**, 333-344.

[14] Grammatikogiannis H. and Stratigea A., 2010. Evaluation Methodology of Alternative Wind Farm Siting Areas (in Greek), *Technika Chronika*, **3**, 77-86.

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Planning of the installation of an offshore wind farm

S. Evangelopoulou[*], E. Loukogeorgaki

Department of Civil Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece.
*Corresponding author: Email: sofia@civil.auth.gr

Abstract

The successful implementation of an Offshore Wind Farm (OWF) project requires the appropriate planning of the whole installation process towards the efficient management of the project's activities and of the corresponding resources (people, materials and equipment). In the present paper, the planning of the installation of a 218 MW OWF in the Greek seas is implemented, aiming at the efficient management and the cost control of the installation process. The installation of the examined OWF is implemented through the development of three different installation scenarios, by modifying: (a) the applied installation method and (b) the characteristics of the installation fleet. In this way, the effect of the two aforementioned parameters on the duration and on the cost of the installation process is examined and demonstrated. Moreover, the effect of the weather conditions on the installation timetable and on the corresponding cost is being investigated.

Keywords: offshore wind farms; installation planning; time schedule; cost control; weather constraints

1. INTRODUCTION

The efficient harnessing and exploitation of the indigenous offshore wind energy potential, directly linked to the long-term strategies, priorities and energy policies of the European Union [1], can contribute significantly to the coverage of the increasing energy demands in European countries [2]. As a result, in recent years the offshore wind energy sector and the Offshore Wind Turbines' (OWTs) technology have been rapidly developed and this fact has resulted to large-scale commercial deployment of Offshore Wind Farms (OWFs), especially in the coastal and offshore areas of Northern Europe [3]. In Greece, contrary to the northern European countries, the investments in the offshore wind energy sector present nowadays only a future goal. This may be attributed to the existence of bureaucracy barriers and strict licensing procedures related to the implementation of OWF projects, as well as to the lack of corresponding know-how and expertise related to the manufacturing and the installation of OWFs.

The successful implementation of OWFs projects, besides the efficient handling of various technical challenges related to the design and the operation of OWTs, requires the appropriate planning of the whole installation process towards the efficient management of the project's activities and of the corresponding resources (people, materials and equipment). Under this framework, the installation process of an OWF has been investigated by various researchers, who presented various aspects of this process (e.g. installation methods, requirements of the installation fleet) [4, 5, 6] or they focused on the optimal planning of the relative marine operations [7]. In all the above studies, specific projects (Cases Studies) were considered, since the activities and the resources (e.g. vessels) of the installation of an OWF depend strongly upon the size of the OWF, the installation depth and the applied configuration of the OWTs' support structure.

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In the present paper, the planning of the installation of a 218 MW OWF in the Greek seas is implemented, aiming at the efficient management and the cost control of the installation process. The OWF is considered to consist of 66 fixed bottom OWTs, with monopile support structures. Initially, the critical parameters of the installation process of an OWF consisting of fixed bottom OWTs are briefly described. Next, the installation of the examined OWF in the Greek seas is implemented through the development of three different installation scenarios, by modifying: (a) the applied installation method and (b) the characteristics of the installation fleet (i.e. type and number of vessels). In this way, the effect of the two aforementioned parameters on the duration and on the cost of the installation process is examined and demonstrated. Moreover, the effect of the weather conditions on the installation timetable and on the corresponding cost is being investigated. This is achieved through the inclusion of weather constraints on the timetable and the calculation of cumulative probabilities related to the project's duration and to the additional installation cost, resulting from the various activities' delays.

2. CRITICAL PARAMETERS OF THE INSTALLATION PROCESS OF AN OWF WITH FIXED BOTTOM OWTs

Based on common practices applied so far in OWFs projects, the installation process of an OWF, consisting of fixed bottom OWTs (e.g. monopile-supported OWTs), includes the following distinctive installation stages (Figure 1): (a) installation of the OWTs' support structure (foundation structure, e.g. monopile, and transition piece), (b) installation of the OWTs' superstructure (tower and Rotor Nacelle Assembly (RNA) including the hub, the blades and the nacelle) and (c) installation of the array and export cables. For installing the OWTs, the aforementioned OWTs' parts are transported from the onshore construction site to the offshore installation area (Figure 1). There are a variety of parameters that affect the duration and the cost of the installation process of an OWF [4, 5, 6, 7]. Among those parameters, the applied installation method, the characteristics of the installation fleet (i.e. type and number of vessels) and the weather conditions are considered in the present paper as the most critical ones.

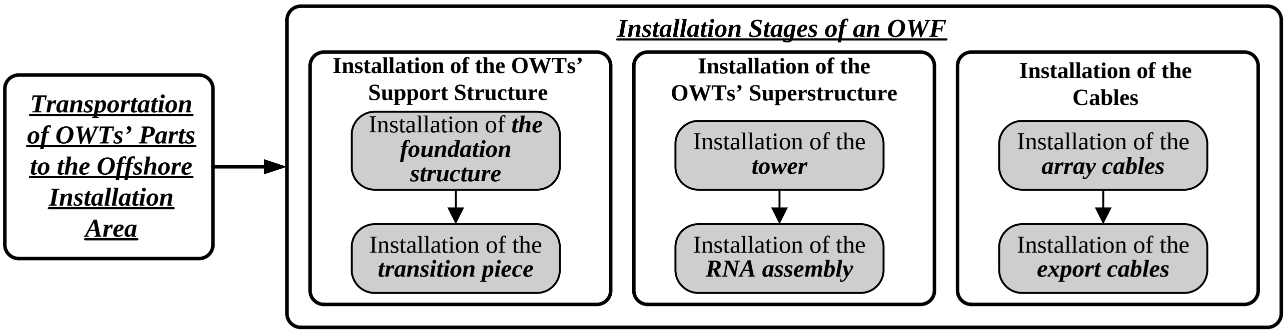


Figure 1. Transportation of OWTs' parts and installation stages of an OWF.

With regard to the first critical parameter, the installation method is related to the applied implementation sequence of the installation stages shown in Figure 1. Specifically, two different installation methods may be defined depending upon the implementation of the installation stages either in series (1st installation method) or in parallel [5] (2nd installation method). In the case of the 1st installation method, the support structures of the OWTs are initially transported and installed in the field. Then, the transportation and the installation of the OWTs' superstructures follow as well as the cables' installation. It is mentioned that the transportation and the installation of the OWTs'

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support structures is usually implemented successively per groups. Each group contains a specific number of support structures depending upon the capabilities of the installation fleet. The same holds for the OWTs' superstructures. The 1st installation method is the simplest one and it is highly recommended for OWFs with a small number of OWTs and/or for cases with limited available resources. As for the 2nd installation method, the support structures and the superstructures of the OWTs are transported and installed in parallel and, then, the cables' installation follows. The above transportation and installation are usually implemented successively for distinctive groups of OWTs, depending again upon the capabilities of the installation fleet. A prerequisite for applying this method is the existence of human resources with high-level expertise, the availability of the installation fleet and the budget availability.

Additionally to the applied installation method, it is straightforward that the installation process of an OWF depends strongly upon the available resources (people, materials and equipment) [7] and their management as well as upon the onshore construction site's (e.g. port) infrastructures and its logistics [8]. Among the above parameters, the characteristics of the installation fleet (i.e. type and number of vessels) have been considered in the present paper as the second critical parameter of the OWFs' installation process. The selection of the vessels' type and number depends upon the size of the OWTs, the applied installation method, the availability of the vessels as well as upon the budget availability.

Finally, with regard to the third critical installation parameter, the existing weather conditions (wind and wave conditions) may reduce the performance of the installation vessels and/or may interrupt the installation process and, therefore, they may impose constraints on the implementation of the transportation of the OWTs' parts as well as on the completion of the activities of the various installation stages (Figure 1). Consequently, the weather conditions may lead to timetable delays and to an increase of the installation cost. In the present paper, the wind velocity 10 m above the mean water level, U_{10}, and the significant wave height, H_s, have been selected as the physical quantities describing the weather conditions. Based on the experience of installed OWFs and taking into account the vessels' size as well as the experience/know-how of the human resources, weather conditions corresponding to $U_{10}\geq7$–10 m/sec and/or $H_s\geq1.5$–3 m may be considered inadequate for the safe implementation of any transportation and installation activity of an OWF project. It is mentioned that in the present paper the threshold values of 7.5 m/sec and 1.5 m for U_{10} and H_s respectively have been taken into account.

3. INSTALLATION OF A 218 MW OWF IN GREEK SEAS

In order to investigate the effect of the critical installation parameters, described in the previous section, on the installation process of an OWF, the case of a 218 MW OWF in the coastal area of Alexandroupoli, in Northern Greece (Figure 2) is taken into account. The project is currently at a status of early planning. The OWF consists of 66 fixed bottom OWTs. The water depth varies between 7.7-28.0 m, while the distance of the OWF from the shore is 5.7 km. The capacity of the OWF can cover the energy demands of 212187 Greek households, i.e. it can cover part of the energy demands of the surrounding onshore areas.

The installation of the examined OWF is implemented through the development of three different installation scenarios, by modifying: (a) the applied installation method (Figure 3) and (b) the characteristics of the installation fleet (i.e. type and number of vessels) (Table 1).

In the case of the installation scenarios No. 1 and No. 2 (Figure 3), the installation stages (Figure 1) are implemented in series (1st installation method, see Section 2). Initially, the OWTs' support structures are transported and installed in the field. The support structure's transportation and installation are implemented successively for 22 distinctive groups of support structures (3 support structures per group). Then, the corresponding export and array cables are installed, while,

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finally, the transportation and the installation of the superstructures are implemented successively for 22 distinctive groups of superstructures (3 superstructures per group). Although the same installation method is applied for both installation scenarios No. 1 and No. 2, the characteristics of the installation fleet are different between these two scenarios. This is shown in Table 1, which includes the type and the number of vessels that are taken into account in the corresponding installation scenarios.



Figure 2. Location of the examined OWF.

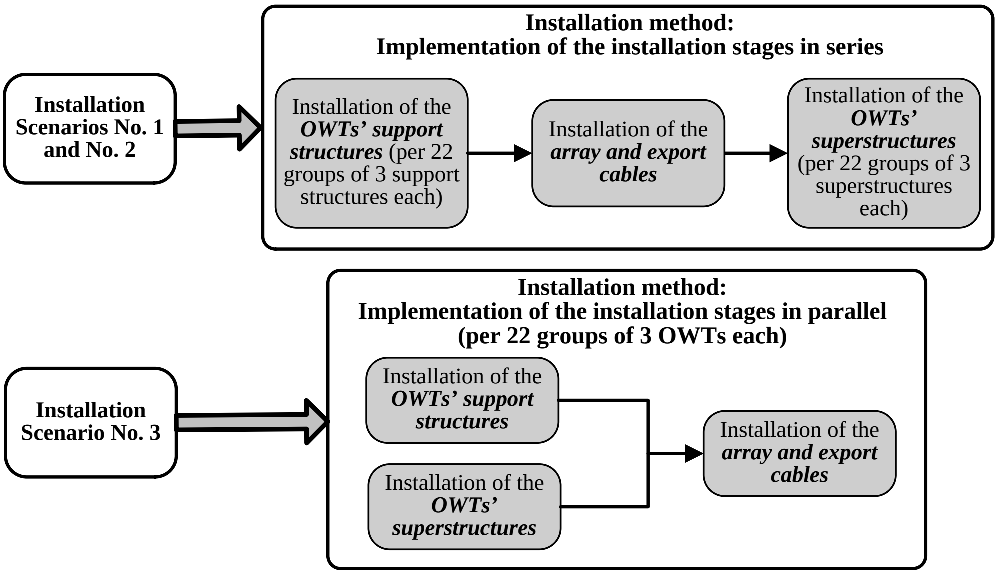


Figure 3. Applied installation methods for the three examined installation scenarios.

In the case of the installation scenario No. 3 (Figure 3), the 2nd installation method described in Section 2 (implementation of installation stages in parallel) is used. This method is applied successively for 22 distinctive groups of OWTs (3 OWTs per group). More specifically, starting with the first OWTs' group, the support structures and the superstructures of the first 3 OWTs are

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transported and installed in parallel and, then, the corresponding cables are being installed. Having finished with the first group of the OWTs, the above installation method is applied successively for the rest 21 OWTs' groups. Table 1 shows the type and the number of vessels considered for the installation scenario No. 3. It should be mentioned that the characteristics of the installation fleet in the case of the installation scenario No. 3 are the same with the ones considered for the installation scenario No. 2.

The duration and the cost of the installation process for all the examined installation scenarios have been initially assessed assuming the existence of good weather conditions during the whole project's duration (no consideration of weather conditions' effect on the project's activities). The scheduling (timetable) of all the required activities and, therefore, the estimation of the project's duration, assuming the existence of good weather conditions, have been implemented using the Microsoft (MS) Project software. For assessing the cost of the installation process, the required cost information (e.g. cost of vessels) has been acquired based on personal communication with managers and engineers of companies specialized on OWFs projects. It is mentioned that both duration and cost have been assessed taking also into account the transportation of the OWTs' parts from the Alexandroupoli's port (Figure 2) to the offshore installation field. For this transportation, the selected vessels (Table 1), expect of the vessels related to the cables, are used. Finally, the effect of the weather conditions on the duration and on the cost of each of the installation scenarios No. 2 and No. 3 has been assessed using COAST (Comprehensive Offshore Analysis and Simulation Tool) developed by Fraunhofer Institute for Wind Energy and Energy System Technology. By including weather constraints on the timetable as obtained from the MS Project software, COAST performs Monte Carlo simulations [9] and enables the calculation of cumulative probabilities related to the project's duration and to the additional installation cost, resulting from the various activities' delays. The data of H_s and U_{10} (time series between 1980 and 2014) at the installation area required in COAST have been acquired from the Hellenic Centre for Marine Research (HCMR). It is mentioned that the timetable included as input in COAST should have activities with finish-to-start connections. This fact imposes a limitation on the connection type between the activities that should be considered in the MS Project software. Finally, in COAST a 24-hours project calendar is taken into account, contrary to MS Project, where a standard 8-hours project calendar is used.

Table 1. Characteristics of the installation fleet for all examined installation scenarios

Installation Scenario No. 1		**Installation Scenario No. 2**		**Installation Scenario No. 3**	
Vessels	**Installation of**	**Vessels**	**Installation of**	**Vessels**	**Installation of**
Barge	Support structure	Jack up foundation vessel	Support structure	Jack up foundation vessel	Support structure
Tug boat 1					
Tug boat 2					
Cable vessel,	Export cables	Cable vessel,	Export cables	Cable vessel	Export cables
Support cable vessel		Support cable vessel		Support cable vessel	
Cable vessel	Array cables	Cable vessel	Array cables	Cable vessel	Array cables
Support cable vessel		Support cable vessel		Support cable vessel	
Jack up turbine vessel	Superstructure	Jack up turbine vessel	Superstructure	Jack up Turbine vessel	Superstructure

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4. RESULTS AND DISCUSSION

Initially, the three examined installation scenarios are analysed assuming the existence of good weather conditions during the whole project's duration (no consideration of weather conditions' effect on the installation process). In this way, the effect of the applied installation method and the characteristics of the installation fleet on the duration and on the cost of the installation process is examined and demonstrated. Then, the existing weather conditions at the installation area are taken into account and the effect of these conditions on the duration and on the cost of installation process is assessed.

4.1 Effect of the installation method and the fleet's characteristics on the installation process

The estimation of the project's duration for all examined installation scenarios is based on the sequence of project's activities and on the connection type between these activities. In the present paper a finish-to-start connection for all activities has been assumed. This assumption is made based on the limitation of COAST, as explained previously in Section 3. A common starting date for all the three examined installation scenarios is taken into account, while the same cost per day has been considered for vessels that are common in two or more installation scenarios. Table 2 shows the duration and the cost calculated for each one of the examined installation scenarios.

Comparing the installation scenarios No. 1 and No. 2 (same installation method, different characteristics of the installation fleet), it is clear that the characteristics of the installation fleet has an impact on the installation cost of the project. Specifically, in the case of scenario No. 2, the use of a jack up foundation vessel for installing the support structures (Table 1) leads to an 11.4% increase of the installation cost compared to the corresponding cost of scenario No. 1. Moreover, the use of the aforementioned specialized vessel does not contribute to the timetable's compression. This may attributed to the fact that in the present paper the same operational time has been considered for both the jack up foundation vessel and for the barge maneuvered and moved by the two tug boats due to lack of corresponding required cost data.

Table 2. Duration and cost for all examined installation scenarios (no consideration of weather conditions' effect)

Installation scenario	Starting date	Finish date	Duration (days)	Installation costs (million €)
No. 1	March 1, 2016	January 10, 2018	487	212.854
No. 2		January 18, 2018	493	237.209
No. 3		June 2, 2017	329	119.399

Focusing on the effect of the applied installation method considering the use of the same installation fleet, the installation scenarios No. 2 (implementation of installation stages in sequence) and No. 3 (implementation of installation stages in parallel) show remarkable differences as far as the project's duration and cost (Table 2). Specifically, the installation method applied in the case of scenario No. 3 enables the more efficient utilization of the assigned resources, namely the jack up foundation vessel and the jack up turbine vessel, as well as the fastest completion of the required installation stages; therefore, the duration of the installation process is significantly decreased (a decrease of 33.3% in the project's duration is achieved compared to the installation scenario No. 2). Considering that the compression of the project's timetable leads to a decrease of the operational and leasing costs of the installation fleet, a straightforward result of all the above is the significant reduction of the installation cost in the case of the installation scenario No. 3 (a decrease of 50.0% approximately in the project's cost is achieved compared to the installation scenario No. 2).

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4.2 Effect of weather conditions on the installation process

The effect of the weather conditions (H_s and U_{10}) on the duration and on the cost of the project is investigated for the installation scenarios No. 2 and No. 3. Based on the Monte Carlo simulations performed in COAST, the cumulative probabilities related to the project's duration and to the additional installation cost, resulting from the various activities' delays, are calculated. The corresponding results are shown in Figure 4.

Considering the cumulative probabilities of the project's duration (Figures 4a and 4b), it should be mentioned that for a 24-hours project calendar considered in COAST the on-time completion of the project (existence of good weather conditions during the whole project's duration) is equal to 159 and 110 days for the installation scenarios No. 2 and No. 3 respectively. The existence of durations larger than the above values corresponds to timetable delays caused by the interruption of the transportation and of the installation activities due to the existence of weather conditions, which are inadequate for the safe implementation of these activities. The aforementioned delays result to an increase of the project's installation cost calculated assuming the existence of good weather conditions (Table 2). Consequently, cumulative probabilities of the additional installation cost can be calculated (Figures 4c and 4d). It is mentioned that the additional cost per day is different between the two examined scenarios ($175X10^3$ € and $120X10^3$ € for installation scenarios No. 2 and No.3 respectively), since the installation activities, where the delays appear are different. This fact is a direct consequence of the consideration of different installation methods in the two examined scenarios. Specifically, in the case of the installation scenario No. 2, the project's delays and, consequently, the additional installation cost are attributed to the existence of a larger operation time for installing the OWTs' support structures. On the contrary, the project's delays and, consequently, the additional installation cost in the case of the installation scenario No. 3 are related to delays on the cables' installation. Based on Figure 4, it is clear that for both installation scenarios, the existing weather conditions have a small effect on the duration and on the cost of the specific project, since the probability of a delayed completion of the project is equal to 3.4% and 2.6% for the installation scenarios No. 2 and No. 3 respectively.

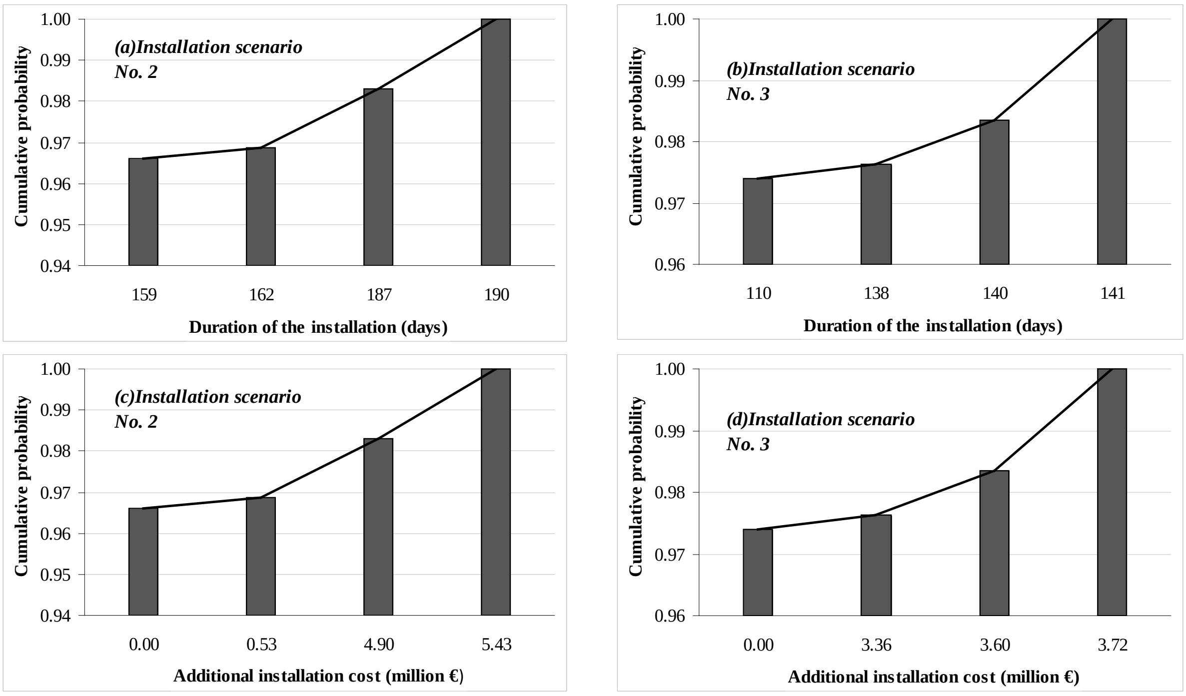


Figure 4. Cumulative probabilities of duration and of additional installation cost for the installation scenarios No. 2 and 3.

Table 3 shows the maximum possible duration and cost of the project for the installation scenarios No. 2 and 3 considering the effect of the weather conditions on the installation process. In the same Table, the duration (use of 24-hour project calendar) and the cost of the project assuming the existence of good weather conditions during the whole project's duration (no consideration of weather conditions' effect) is also shown for comparison reasons.

Table 3. Duration (24-hour project calendar) and cost for installation scenarios No. 2 and No. 3 without and by considering weather conditions' effect

	No consideration of weather conditions' effect		**Consideration of weather conditions' effect**		
Installation scenario	**Duration (days)**	**Installation cost (million €)**	**Maximum delay (days)**	**Maximum duration (days)**	**Maximum installation cost (million €)**
No. 2	159	237.209	31	190	242.634
No. 3	110	119.399	31	141	123.119

It can been seen that the weather conditions may lead to an increase of the duration of the installation process approximately up to 19% (max delay equal to 31 days) and up to 28% (max delay equal to 31 days) for the installation scenario No. 2 and No. 3 respectively. As a result of this delay, a maximum possible increase of the installation cost equal to 2.3% and 3.1% for the installation scenario No. 2 and No. 3 respectively is observed compared to the installation cost calculated assuming the existence of good weather conditions.

CONCLUSIONS

In the present paper, the planning of the installation of a 218 MW OWF in the Greek seas is implemented, aiming at the investigation of critical parameters on the corresponding installation process. For the examined OWF project, the applied installation method, contrary to the characteristics of the installation fleet, has a significant impact on both the duration and the cost of the installation process. Specifically, the implementation of the OWF's installation stages in parallel enables a more efficient utilization of the assigned resources; therefore, it leads to a significant decrease of both the duration and the cost of the installation process. However, it is mentioned that this method requires high level of expertise, experience on similar projects and availability of the required installation fleet. Based on the above, it is clear that the applied installation method and the appropriate scheduling of the installation activities are crucial towards the efficient management and the cost control of an OWF's installation process. With regard to the weather conditions, it is clear that irrespectively of the applied installation method, the existing weather conditions for the examined OWF project have a small effect on its duration and its cost, since the probabilities of a delayed completion are quite small. In any case, cumulative probabilities of the project's duration and of the additional installation cost resulting from the consideration of weather conditions may contribute to the effective project management of an OWF installation.

References

[1] European Renewable Energy Council, 2010. *Renewable energy in Europe: Markets, trends and technologies*. 2nd ed., Earthscan, Washington and London.

[2] European Wind Energy Technology Platform, 2014. Strategic Research Agenda / Market Deployment Strategy (SRA/MDS). European Wind Energy Technology Platform.

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ISBN: 978-960-6865-94-7

[3] European Wind Energy Association (EWEA), 2016. The European offshore wind industry - Key trends and statistics 2015. EWEA.
[4] Li L. and Ren J., 2010. Offshore wind turbines and their installation. *Proceedings of the 2010 International Conference on Innovative Computing and Communication and 2010 Asia-Pacific Conference on Information Technology and Ocean Engineering (CICC-ITOE 2010)*, January 30-31, Macao, China, 248-251.
[5] Wang W., Bai Y., 2010. Investigation on installation of offshore wind turbines. *Journal of Marine Science and Application*, **9**, 175-180.
[6] Ait Alla A., Quandt M. and Lütjen, M., 2013.Aggregate installation planning of offshore wind farms. *Recent Advances in Eletrical & Computer Engineering: Proceedings of the 7th International Conference on Communications and Information Technology (CIT 13 - WSEAS)* January 30-February 1, Cambridge, MA, USA, 130-135.
[7] Uraz E., 2011. *Offshore wind turbine transportation & installation analyses: Planning optimal marine operations for offshore wind projects.* Master Thesis, Gotland University, Visby, Sweden.
[8] Lütjen M. and Karimi H.R., 2012. Approach of a port inventory control system for the offshore installation of wind turbines. *Proceedings of the 22nd International Offshore and Polar Engineering Conference (ISOPE 2012)*, June 17-22, Rhodes, Greece, Vol. 1, 502-508.
[9] Tyapin I., Hovland G. and Jorde J., 2011. Comparison of Markov theory and Monte Carlo simulations for analysis of marine operations related to installation of an offshore wind turbine. *Proceedings of the 24th International Congress and Exhibition on Condition Monitoring and Diagnostic Engineering Management (COMADEM)*, May 30 - June 1, Stavanger, Norway.

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Environmental Communication and Education

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XIII

Online M.S. environmental engineering programs – The University of New Haven (UNH) experience

E. Hadnagy[1], B. Riedinger[2], J. Vilberg[2], A. Koutsospyros[1*]

[1] Department of Civil and Environmental Engineering, University of New Haven, West Haven, CT 06516, USA.
[2] Office of eLearning, University of New Haven, West Haven, CT 06516, USA.
*Corresponding author: Email: azyx56@gmail.com

Abstract

In the last decade the world has witnessed an unprecedented growth in distance learning methods extending throughout the entire education continuum (elementary, continuing, undergraduate, and graduate). More than ever, innovative e-learning instructional technologies are used not only for online instruction but have permeated the traditional classroom to create novel hybrid onground/online learning environments. In 2011, the number of students taking at least one online course exceeded one-third of the total US higher education enrollment and continues to grow. In 2015, the University of New Haven launched its first engineering fully online graduate program leading to the M.S. in Environmental Engineering (M.S. EnvE). The M.S. EnvE, established in the early 70s, is one of the first programs of its kind in the State of Connecticut that, for over 40 years, has produced graduates who embarked in successful careers and became leaders in major consulting firms, the industry, the public sector, and academia. The new online program builds on the long tradition of excellence of the on-ground program and aims to reach working professionals who seek advancement and value independent and life-long learning. The work presented herein provides an overview of the new educational paradigm of online education, compares and contrasts two fundamental modes of online instruction (synchronous vs. asynchronous), and teaching and learning in on-ground and online environments. Furthermore, the basic features of the UNH online M.S. EnvE are disseminated, including the program structure and curriculum, institutional support structures, instructor training, examples of instructional activities, and operational challenges and experiences.

Keywords: online programs; synchronous; asynchronous; e-learning; environmental engineering.

1. THE EVOLUTION AND PROLIFERATION OF e-LEARNING

The advent of the Information Age has brought about profound changes in economy, society, and culture. To effectively function in the new era individuals must possess a dynamic and multi-faceted set of attributes (often referred to as 21st Century Skills) for "employment, citizenship, and self-actualization" [1]. Although several groups have contributed a variety of skill lists the one by Partnership for 21st Century Skills is commonly cited [2]. Accordingly, three major groups of skills are identified: 1) Learning and Innovation Skills, 2) Information, Media and Technology Skills and 3) Life and Career Skills. In addition, to promote and communicate knowledge of their specific academic discipline at a higher level, 21st century learners must acquire a variety of interdisciplinary skills including global awareness, financial/–economic/business/entrepreneurial, civic, health, and environmental literacy [2]. This diverse framework of competencies cannot be static and must be adaptive to a rapidly evolving information and communication technologies (ICT) [3].

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To help students attain these competencies the education system must embrace a paradigm shift that relocates the center of its attention to learning [4]. This transformation necessitates a drastic reinvention of the role of teachers, learners, curricula and delivery, and media applications [5]. Central to these radical changes sweeping post-secondary education is a new learning environment where the student is transformed from a passive, dependent, solitary individual to an active, independent, collaborative learner, capable of learning to learn/think/create/communicate and producing rather than reproducing knowledge. In the meantime, the evolution of ICT has created an enormous variety of educational applications that loosen the spatial-temporal confines of the traditional classroom and transform it to an interactive node of the information superhighway system. The "new classroom" is now open not only to the real but also to the digital world. Within this context, the instructor functions not as a conveyor of knowledge or a controller of the learning process but rather as a facilitator of knowledge and a creator of a learning environment. Today, novel instructional scenarios seek to cast interactive, experiential, and exploratory rather than didactic and expository actors; this transition is often epitomized by the expression "from a sage on the stage to a guide on the side" [6].

These innovations have spurred an unprecedented advance of e-learning (a.k.a. distance education/learning) programs that embody emerging learning environments capable of supplementing or replacing traditional face-to-face (F2F) instruction [7]. These cover the entire spectrum from none to fully online distance learning and include hybrid learning, blended online (BOL), and massively open online courses (MOOC). Fully online distance learning may be delivered in one of two modes, synchronous or asynchronous. Synchronous online learning requires the simultaneous "presence" of participants (students and instructor) via a variety of remote audio-visual conferencing technologies in a simulated virtual classroom environment. Asynchronous is student centered learning based on the constructivist educational theory. This approach relies on independent learning combined with peer-to-peer interactions that build an asynchronous learning network (ALN) [8]. Although, synchronous and asynchronous e-learning methods support different purposes [9], for a number of reasons beyond the scope of this review, asynchronous is the preferred mode for most online post-secondary programs in the U.S. expected to attain mainstream status by 2020 [10]. Combinations of asynchronous and synchronous online features (i.e. BOL) as well as traditional F2F and online instruction (i.e. hybrid) are also practiced. MOOCs are online courses targeting unlimited participation and open access via the internet. The users (students, teaching assistants, instructors) form an interactive user network and share course resources, views, and opinions. The popularity and use of MOOCS has peaked in 2012 and although still available today, interest in them has tapered off [11].

Enrollment data verify the explosive development of online education. Since 2004, when online education statistical records have been compiled, enrollment in online courses and programs has increased exponentially. In less than ten years (2003-2012), the number of students enrolled in at least one online course increased from 1.9 to 6.7 million students, the latter number representing more than one third of the total enrollment in U.S. Higher Education institutions (32.5%) [12, 13]. These numbers indicate that online education is attaining a mainstream status and is, according to 69.1% of academic leaders, is critical to long-term strategy of their institutions [13]. Engineering online programs are lagging behind other disciplines primarily because of the inevitable reliance on laboratory courses and mathematics/science fundamental subjects that are challenging for online instruction. However, for M.S. level engineering programs, there are fewer perceived barriers to online instruction since they do not rely as much on laboratories, students have already mastered basic mathematical and science skills, and the program credit requirements are significantly lower [14]. For these reasons, M.S. level programs are often considered as the gate of entrance to online education for many engineering institutions of higher learning.

The work reported here disseminates the academic and institutional steps and pathway from conception to creation and establishment of the online M.S. in Environmental Engineering at the

UNH. The basic online education philosophy, the fundamental governing principles and standards for online course development are discussed. In addition, the faculty technical and instructional training programs are presented. Finally, challenges and lessons learned during the first year of program operation are reviewed.

2. e-LEARNING AT THE UNH

2.1 Institutional Profile

The UNH is a private, comprehensive institution of higher education with its main campus located in West Haven, CT, USA. The university, established in 1920, moved to its current main campus location in 1960 and also operates several other campus locations throughout the state of CT (Orange, Old Lyme, New London), in San Francisco, CA, Albuquerque, NM, and a satellite campus in Tuscany, Italy. Currently, student enrollment stands at about 6,800 students (5,000 undergraduate and nearly 1,800 graduate students) with international students making up 10% of the total student population. The UNH offers about 80 undergraduate and graduate degree programs, the latter primarily at the M.S. level, in engineering, criminal justice and forensic sciences, business, natural and social sciences, and arts. The institution's rich tradition in professional education made it a natural candidate to enter the online education market and thus expand its reach beyond the local commutable areas. Currently, UNH offers four totally online programs: a M.S. in Criminal Justice, a M.S. in Emergency Management, the M.S. EnvE, and a B.S. in Professional Studies.

In the sections immediately following various aspects of online education at the UNH are presented. The UNH approach to online course development is illustrated graphically in Figure 1.

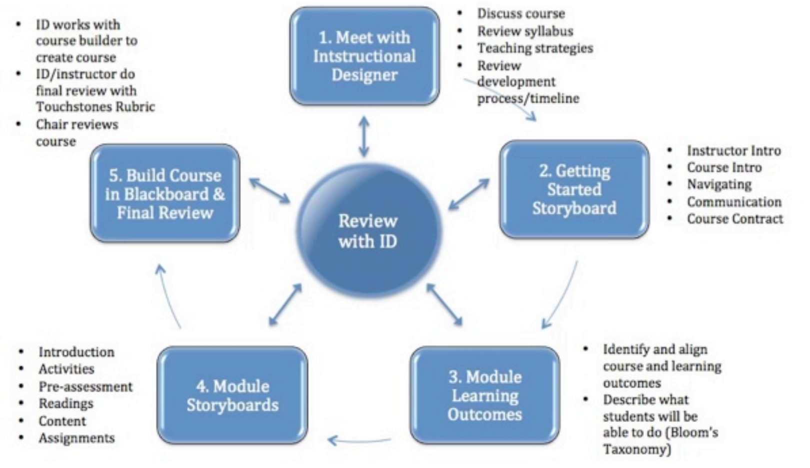


Figure 1. The UNH online course development process.

2.2 e-Learning foundations at the UNH

Neuroscience, education research, and universal design principles are the foundation of course development for the online graduate Environmental Engineering program at the UNH. This combination ensures that sound learning research drives the creation of activities and assessments, the presentation of content, and the selection of technical tools. The UNH Touchstones, the university's online development standards, are based on these principles and research, and are used during course development and as the basis for course evaluation when development is complete. Training for faculty who will develop or teach online courses also is based on these same principles

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and research. The transition from classroom to online teaching provides a unique opportunity for faculty to learn effective teaching strategies in the new learning environment. The UNH Office of eLearning has developed a framework to support instructors who are designing and teaching online courses. The framework is based upon established, research-based instructional design practices [15].

2.3 Faculty training

Since UNH has an instructional design staff, faculty training focuses on how to use the course management system for teaching rather than course building. The Office of eLearning provides a combination of one-on-one technical training (face-to-face or via synchronous web meeting) and an asynchronous, fully online course on the pedagogical aspects of teaching online. Prior to taking the online course, faculty members learn how to navigate Blackboard (Bb), the university's course management system, and use basic tools such as the discussion board, assignment tool, and blog. They also learn how to create audio and video files as well as other instructional, and communication applications. After the technical training, faculty are enrolled in the Foundations of Online Teaching and Learning course, providing them with an online student experience as they learn about online pedagogy. Because faculty members traditionally have little or no formal professional training in teaching, the Foundations course provides a critical focus on online teaching strategies and student-centered learning. The outcomes of the Foundations course are shown in Table 1.

Table 1. Outcomes of the UNH Foundations course

After completion of the Foundations course, faculty are expected to be able to:			
1.	Align course and module outcomes with online assignments and assessments	**6.**	Create an online community of learners
2.	Align online teaching tools and outcomes	**7.**	Communicate effectively in the online environment
3.	Compare and contrast online and on-ground teaching and learning	**8.**	Provide effective formative and summative online feedback
4.	Select the appropriate pedagogical approach(es) for their online course	**9.**	Create a safe, interactive, and engaging environment for learning and discussion
5.	Develop an online teaching presence	**10.**	Design authentic online learning assignments and assessments

During the first week of the course, faculty practice creating videos and building online community through an introductions forum and discussion of teaching styles and philosophies. This informal, ungraded week is followed by four intensive weeks of graded collaborative and individual assignments. The last two weeks are reserved for revisions and completion of a three- to five-page online teaching philosophy.

2.4 The touchstones

The UNH Touchstones are the standards used in online course development and assessment. They are based on research on learning effectiveness and are designed to ensure that our courses meet all state, federal, and regional accreditation requirements. In addition, the standards ensure that the courses meet student-centered learning goals [16]. There are five assessment areas: Learning Outcomes, Student Information, Student Navigation, Learning Environment, and Student Learning.

Learning Outcomes: Learning outcomes for each module in the course must be clearly written, measurable, aligned with course outcomes and module assessments and must show progression toward higher order learning [17].

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Student Information: Most of the requirements in the student information and navigation areas are covered in the UNH-branded Bb course template. Items include detailed information on policies and procedures, such as academic integrity; consistent course navigation design that conforms to universal design standards; a student contract; discussion forums for course questions and community building; and information on student services such as library, counseling, and technical assistance. A syllabus template also is included in the main course template.

Student Navigation: Introductory, contextual, and transitional text also helps guide students through the course material, which is chunked and scaffolded [18] to optimize learning.

Learning Environment: Requirements for the learning environment include: instructor and student introductions (preferably through video); an honor pledge, modeling and instruction for netiquette and academic discourse, a statement of instructor response time of 24 hours or less to student questions and regular instructor interaction with students through discussion forums and announcements.

Student Learning: Student learning requirements include: pre- and post-assessments; timely formative feedback; authentic, multimodal, learner-centered assignments and assessments, collaborative and reflective assignments; classroom assessment techniques [19]; information literacy; and metacognitive approaches to assignment design.

2.5 The template and design process

Each course is constructed in a Bb template that provides a consistent navigation structure, essential information about UNH policies and student services, a syllabus template, and areas in which to create course-specific content and opportunities for prior knowledge assessment, collaboration, and reflection. The design process is a collaborative effort; the development team consists of the instructional designer and the faculty member, working in cooperation with the IT staff, librarians, program chairs and other faculty as needed. Course development begins at least six months before a course is scheduled to be offered for the first time. The process begins with a meeting between the faculty member and the instructional designer, who creates a timeline for development, which is then attached to the faculty member's memorandum of agreement for course development. Faculty members receive a stipend after the course is completed and reviewed against the Touchstones rubric. Using the UNH templates to guide the design process, faculty members begin their course development by identifying course and learning outcomes. Online courses have the same course outcomes as face-to-face versions of the course. Learning outcomes for each of the weekly course modules are created based on the course outcomes. Activities and assessments are then developed that align with the outcomes for each module. This process is known as "backward design" [20].

3. THE ONLINE M.S. ENVE AT UNH

3.1 Program description

The fully online M.S. EnvE program has been launched in January 2015. The online program is based on the UNH's well-known and respected on-ground M.S. EnvE program established in the early 70's. Both programs, offered by the Department of Civil and Environmental Engineering, require the completion of 30 credits.

Online courses are offered in 5 convenient 7.5- or 6-week long terms, during the academic year and the summer, respectively (2 terms in the spring, 1 in the summer, and 2 in the fall) at one course per term allowing students to complete the program in as little as 2 years. To provide flexibility for working professionals not able to commit to taking courses throughout the year, a maximum program completion period of 5 years is allowed. The online M.S. EnvE program was designed for working professionals and features a fully supported online learning environment. Courses, offered in an asynchronous mode, can be completed fully online using Blackboard (Bb), the same

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instructional platform used UNH-wide to augment on-ground courses with online instructional elements. Furthermore, online courses are developed with the help of trained instructional designers with a background in education, educational technology, and online course delivery. All online courses feature full technical support for issues associated with the use Bb and other ICTs.

As of March 2016, seven online M.S. EnvE courses have been successfully delivered (the program was launched in January 2015), while the 8th course is currently in progress. In addition, two more courses are under development and will be offered during the fall 2016 semester. This will mark the completion of the first full course cycle and possibly the first program graduates. As enrollment increases and once the program has been well established, additional course offerings will be planned and implemented.

3.1 The curriculum

The online M.S. EnvE program offers 10 3-credit courses in various areas of environmental and water resources engineering, and in environmental law (see Table 1). Students also have the option to work on a Research Project (CIVL 6690), or an Independent Study course (CIVL 6695) instead of one of the 10 courses shown in Table 2.

Table 2. M.S. EnvE online courses

Course Code	Course Title	Course Code	Course Title
CIVL 6601	Physical-Chemical Treatment of Aqueous Wastes	CIVL 6614	Surface Water Quality Management
CIVL 6602	Biological Treatment of Aqueous Wastes	CIVL 6618	Hazardous Waste Treatment
CIVL 6603	Contaminant Fate and Transport in the Environment	CIVL 6623	Open Channel Hydraulics
CIVL 6605	Solid Waste Management	CIVL 6661	Air Pollution Fundamentals
CIVL 6606	Environmental Law and Legislation	CIVL 6690	Research Project
CIVL 6610	Pollution Prevention Management Technologies	CIVL 6695	Independent Study I

The content of all online courses is based on the on-ground version of the course, however, course delivery methods and assignment types may vary considerably. For example, online course content is delivered asynchronously using a variety of methods that include written module outlines, PowerPoint presentations with voice-over recordings, video recordings of problem solving exercises, software demonstrations, and open source videos available on the internet. Assignments for online courses are typically more writing intensive and include posts to weekly discussion boards, weekly journal entries to document one's study process or challenges encountered, quizzes, problem sets, and tasks associated with the term project.

A key component in all online courses is that instructors facilitate the establishment of an active and engaged learning community. This is achieved by video introductions, frequent instructor feedback, discussion boards, journals, and communication messaging. Course material is broken down into weekly modules that students complete at their own pace. However, assignments associated with a given module have to be submitted by mid- or end-of-the-week deadlines.

3.2. The faculty and the students

The online M.S. EnvE courses are taught by the same faculty members (full-time or adjunct) as their on-ground counterparts. All full-time faculty members have a terminal degree and adjunct faculty members are all successful practitioners with significant experience in their respective fields. All faculty must complete the foundations course prior to developing or teaching an online course.

Online students come from a variety of science backgrounds including environmental science, chemistry, physics, biology, geology, soil science, marine science, and environmental health. Students with a non-civil or environmental engineering background are required to complete certain undergraduate courses in mathematics, environmental or water resources engineering prior to matriculation. Relevant work experience is also accepted in lieu of some of these prerequisite courses. The majority of the online students are working professionals with 2-7 years of professional experience in environmental engineering or related areas who continue their daytime jobs while taking courses. Some applicants have at least 10 years of work experience past the B.S. degree, but not necessarily in the field of environmental engineering. Finally, a small number of applicants have over 20 or 25 years of work experience in environmental engineering or related areas. These working professionals choose to take a full course load (i.e. they complete all courses offered in a given year) or they register for 2-3 course per year depending on their time availability and financial situation. Most students either apply for federal financial aid or employer tuition reimbursement programs. The program draws applicants from many parts of the U.S. (i.e. NY, PA, NJ, VA, OH, MI, GA, CO, WA). In addition, certain students of the on-ground M.S. EnvE and the M.S. in Environmental Science programs are allowed to register for up to 2 online courses while at UNH. A decision is based on uniform selection criteria (minimum GPA of 3.0, demonstrated time management, and self-learning skills) and an interview with a faculty member to discuss differences in expectations in on-ground and online courses.

3.3 Institutional support structures

The program, department, and the College

The online M.S. EnvE program is administered by the Department of Civil and Environmental Engineering at the Tagliatela College of Engineering at the UNH. One of the full time faculty members serves as the coordinator of the online M.S. EnvE program. The program coordinator's duties include meeting with prospective students, making acceptance decisions, and serving as the academic advisor for students enrolled in the program. Additional duties include course scheduling, adjunct staffing, and interacting with the various offices that are involved in online program planning, delivery, and student recruitment and retention related activities. Finally, the College of Engineering provides one teaching assistant to the Department to support the online M.S. EnvE program.

Graduate admissions

The office of Graduate Admissions oversees program marketing, recruitment, and admission related activities. Prospective students can contact a designated enrollment counselor who guides them through the application process. The counselor also directs students to the program coordinator as needed, typically for inquiries related to the academics. In addition, the director of Graduate Admissions serves as the primary contact person for online students regarding any student support related issues, such as matters concerning registration or financial aid.

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3.4 Operational challenges and lessons learned

Recruitment

Program marketing and student recruitment is currently overseen by Graduate Admissions. Program faculty also contributes to recruitment efforts by participating in open houses, communicating with prospective students, and by professional networking. The Admissions office has implemented a targeted marketing campaign for the online program, but despite all efforts, the number of applicants has remained below the target level of 15 students/class during the first year of program operation. As of February 2016, there are 8 students in the online M.S. EnvE program while another 5 students are in various stages of satisfying conditional admission prerequisites. After the first year of operation, under enrolment is a concern but not a threat for long term program stability and sustainability as the establishment of similar online programs is known to take, at the very least, 2-3 years. Considering this, the program still holds a great potential and provides the UNH with a unique opportunity to remain an important participant in a niche academic market.

Student support structure

For on-ground students, the interaction with the Admissions office typically ends upon acceptance into a program. Instead, there are several other offices that service students on a variety of issues, collectively termed student support services. The Graduate Student Services Office organizes the graduate student orientation and also provides a "road map" for new graduate students introducing various student support offices and services. Some of the support offices, commonly used by online students, include the Financial Aid, the Registrar's, and the IT Offices. The challenge faced by online programs is that the university has not created a parallel structure for online student support services similar to the one existing for on-ground students to this date. That is expected to change as more online programs are established and administered.

Lessons learned

January 2016 marked the completion of the first year of online program operation, a milestone that prompts for reflection, informal evaluation and discussion of the experiences, achievements, and challenges. A formal program assessment will be conducted in January 2017 soon after completion of the first program cycle and the graduation of the first class. A brief summary of informal observations, perceptions, opinions, and comments regarding various program aspects by faculty and students is provided below:

- Students and faculty agree that although there are fundamental differences compared to F2F instruction, the online environment provides ample opportunities for effective learning.
- Faculty participating as instructors in the online program:
    - Feel that online courses proved to be more demanding than F2F courses in terms of effort and time required for preparation;
    - View online instruction very enthusiastically;
    - Value the online experience highly;
    - Consider it as an opportunity to reinvigorate their teaching interest;
    - Contemplate that the online environment can act as a motivational force behind the adaptation of new instructional tools and teaching techniques to enrich their F2F courses.
- Students in the online program:
    - Appreciate the greater number and diversity of instructor and peer review performance assessment opportunities in online classes;
    - Value highly online discussions on technical, social, economic, and environmental aspects of technology;
    - Believe the online environment provides more opportunities for group work;
    - Feel they learn equally well or better in an online environment compared to F2F classes;

- Consider that the online environment offers more opportunities to improve social, communication, and leadership skills.

4. CONCLUSIONS

In the last decade the world has witnessed an explosive growth of online programs which in combination with the rapidly evolving ICT have led to innovative e-learning instruction practices. These new e-learning environments require a drastic reinvention of the role of teachers, learners, curricula, delivery, and media applications. Central to the new e-learning environments are neuroscience research and constructivist educational theories. These developments along with universal design principles are the foundation of course development for the online graduate EnvE program at UNH. Training for faculty who develop or teach online courses also is based on these same principles and research. The transition from classroom to online teaching provides a unique opportunity for faculty to learn effective teaching strategies in the new learning environment. The completion of the first year of administering the M.S. EnvE program has proved to generate a positive experience for faculty and students.

References

[1] http://www.gse.harvard.edu/~dedech/Dede_21stC-skills_semi-final.pdf (accessed March 12th, 2016).

[2] http://www.p21.org/storage/documents/aacte_p21_whitepaper2010.pdf, (accessed March 12th, 2016).

[3] Leu, D.J., Forzani, E., Rhoads, C., Maykel, C., Kennedy, C., & Timbrell, N., 2015. The new literacies of online research and comprehension: Rethinking the reading achievement gap. *Reading Research Quarterly*, **50(1)**, 1-23.

[4] Smolin, L. I., & Lawless, K. A., 2003. Becoming literate in the technological age: New responsibilities and tools for teachers. *The Reading Teacher*, **56(6)**, 570–577.

[5] Tapscott, D. and Williams, A. D., 2010. Innovating the 21st-Century University: It's Time! *EDUCAUSE Review*, **45(1)**, 16-29.

[6] http://er.educause.edu/~/media/files/article-downloads/erm0051.pdf (accessed March 5th, 2016).

[7] Boling, E.C., Hough M., Krinsky H., Saleem H., Stevens M., 2012. Cutting the distance in distance education: Perspectives on what promotes positive, online learning experiences, *Internet and Higher Education*, **15**, 118–126.

[8] Bourne, J., Harris, D., Mayadas, F., 2005. Online Engineering Education: Learning Anywhere, Anytime, *Journal of Engineering Education*, **94(1)**, 131-146.

[9] Hrastinski, S., 2008. A study of asynchronous and synchronous e-learning methods discovered that each supports different purposes. *EDUCAUSE Quarterly*, **4**, 51-55.

[10] Sener J., 2010. Why online education will attain full scale. *Journal of Asynchronous Learning Networks*, **14(4)**, 3-16.

[11] Zemsky, R., 2014. With a MOOC MOOC here and a MOOC MOOC there, here a MOOC, there a MOOC, everywhere a MOOC MOOC. *Journal of General Education*, **63(4)**, 237–243.

[12] http://www.onlinelearningsurvey.com/reports/changingcourse.pdf (accessed March 10th, 2016.

[13] http://wcet.wiche.edu/sites/default/files/WCETDistanceEducationEnrollmentReport2016.pdf (accessed March 10, 2016).

[14] http://digitalcommons.olin.edu/cgi/viewcontent.cgi?article=1003&context=facpub_2005 (accessed April, 2, 2016.

[15] Reigeluth, C. ,1999. *Instructional-design Theories and Models: A New Paradigm of Instructional Theory*. Volume 2, Lawrence Erlbaum Associates. Inc., New Jersey.

[16] Knowlton, D. S., 2000. A Theoretical Framework for the Online Classroom: A Defense and Delineation of a Student-Centered Pedagogy. *New Directions for Teaching and Learning*, **2000(84)**, 5-14.

[17] Anderson, L.W., Krathwohl, D.R., Airasian, P.W., Cruikshank, K.A., Mayer, R.E., Pintrich, P.R., Raths, J., Wittrock, M.C., 2001. *A Taxonomy for Learning, Teaching, and Assessing: A revision of Bloom's Taxonomy of Educational Objectives*. Pearson, Allyn & Bacon, New York.

[18] Vygotsky, L.S. (1978). In M. Cole, V. John-Steiner, S. Scribner and E. Souberman, (Eds.), *Mind in society—The development of higher psychological processes*. Harvard University Press, Cambridge.

[19] Angelo, T.A., & Cross, K.P., 1993. *Classroom assessment techniques: A handbook for college teachers*. 2nd ed., Jossey-Bass, San Francisco.

[20] Wiggins, G. P., McTighe, J., Kiernan, L. J., Frost, F., & Association for Supervision and Curriculum Development. (1998). *Understanding by design*. Alexandria, Va: Association for Supervision and Curriculum Development.

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Environmental sensitivity of college students

A. Vamvakari, R. Zarkaveli, C. Skanavis*

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
* Corresponding author: Email: cskanav@aegean.gr

Abstract

At the Earth Summit (1992), in Rio de Janeiro, a set of principles defining the rights of people to development as well as their responsibilities to safeguard the common environment was adopted. That was the time the issue of "sustainable development" made its appearance. Universities around the world have taken the task to promote responsible environmental behavior in their student populations. This research attempts to record the environmental beat of the students at the University of Aegean at Mytilene, in Lesvos Island, Greece. A questionnaire was administered to a sample of 300 students and the collected results were assessed. The purpose of this study is to examine if students of higher education are environmentally active both at campus and their local community. The results will give information as far as what actions are needed in order universities to enhance college students' responsible environmental behavior and to support them as active citizens.

Keywords: environmental sensitivity; college students; sustainable behavior; environmental education; sustainable development, Greece

INTRODUCTION

Sustainability issues in higher educational institutions have attracted increasing levels of attention from both the public and policy makers in recent decades. A number of previous studies have called for a more comprehensive integration of sustainable development into mainstream university operations and curricula [1]. According to Milutinovic and Nikoli [1], the vision of sustainable development in higher education, is a world where everyone has the opportunity to benefit from a quality education and learn the values, behaviors and lifestyles required for a sustainable future and for positive societal transformation. Nevertheless, sustainable development in higher education is still far from being integrated into a holistic and functional manner by university administrators [1]. The purpose of this research is to determine the kind of relationship existing between different demographic factors and the students' perception as members of the university community. In this study sampling research was chosen. Using this type of research a coincidencesample of the population was tested in terms of how students' lifestyle highlights their environmental consciousness.

Education effect in sustainable development

Sustainable development (SD), according to the 1987 United Nations World Commission on Environment and Development, is "meeting the needs of the present without compromising the ability of future generations to meet their own needs" [2]. Sustainable development and the interplay between its ecological, social, and economic dimensions can be regarded as a highly complex task. As a logical consequence, educating for sustainable development also has a complex character [3]. Campus sustainability has become an issue of global concern for university policy makers and planners as result of the realization of the impacts the activities and operations that

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universities have on the environment [4]. Universities can nowadays be regarded as ‘small cities’ due to their population size, and the various complex activities taking place in campuses, which have some serious direct and indirect impacts on the environment [4]. A sustainable university is defined by Habib et al. [4] as ‘‘A higher educational institution, as a whole or as a part, that addresses, involves and promotes, on a regional or a global level, the minimization of negative environmental, economic, societal, and health effects generated in the use of their resources in order to fulfill its functions of teaching, research, outreach and partnership, and stewardship in ways to help society make the transition to sustainable lifestyles’’. We are of the opinion that a sustainable university campus should be a healthy campus environment, with a prosperous economy through energy and resource conservation, waste reduction and an efficient environmental management, that promotes equity and social justice in its affairs and export these values at community, at national and global levels [4].

Sustainable development initiatives in higher education

Both theoretical literature and practical experiences reveal that institutions of higher education can contribute to such sustainable development initiatives in many ways [5]. Over the past decade, many universities have taken a more responsible approach to managing their environmental performance and improvement. This is not isolated to a single country or region, but has been particularly prominent in Europe, USA, Canada as well as in Australia, Asia, South America and Africa [6]. University of Minessota supports sustainable development by directing the University’s resources towards addressing community- identified issues on an on-going, long-term basis [7]. The Halifax Declaration was launched in December 1991 at Halifax, Canada. The declaration underscores the roles and responsibilities of universities in improving the capacity of the citizens of all countries to address environmental and development issues, such as the continuing wide-spread degradation of the earth’s environment, the pervasive influence of poverty on the process, and the devastating effects of unsustainable environmental practices [8]. The Co-operation Programme in Europe for Research on Nature and Industry through the Co-ordinated University Studies (COPERNICUS) Charter was launched in Geneva, Switzerland in May 1994. The Charter is an inter-university, co-operation programme focused upon the environment and SD. It encompasses more than 320 European universities [8]. Santa Clara University created the Office of Sustainability in October 2008 to handle related issues on campus, and support and create further initiatives and efforts [2]. It adopted a Sustainability Policy in 2004 where former President Paul Locatelli, S.J., “devoted the university to sustainability through stewardship, education and outreach”. He then signed the American College and University Presidents Climate Commitment in 2007, aiming to become a climate neutral campus. The university also completed its first Campus Sustainability Assessment in 2007 [2].

The role of universities in sustainable development

As shown by the United Nations' Decade of Education for Sustainable Development (2005–2014), it is clear that today all education institutions – higher education (HE) included – have to find their role in relation to SD. The contribution of Universities to sustainability is increasingly being expressed through the publication and adoption of various strategies and declarations at international, regional and University level [9]. It is widely accepted that universities play an important role in sustainability across the world, providing a vehicle for development. Higher education has a unique academic freedom and a critical mass with diverse skills for developing new ideas in order to "help" the society, challenge and participate in adventurous experimentation to achieve "sustainable living" [10]. Universities educate people who would later on develop and manage social institutions, for that reason, universities bear profound responsibilities to increase the awareness, knowledge, technology and tools to create an environmentally sustainable future [10]. Universities are the pioneers of the academic world and can be a visionary cradle and integrity pole

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and wisdom [10]. An inclusion of sustainable development into university's main activities embraces: education, research, and outreach. Higher education represents one of the most powerful tools when approaching sustainable development because it has academic freedom, the diversity of skills and knowledge for developing new ideas, the ability to comment on society and its challenges, and to engage in experimentation regarding sustainable living [11]. Universities provide the necessary basis for research and education. However their third roleoften referred, as ‘engagement’ is also quite instrumental, signifying a two-way interaction, giving and receiving knowledge. This alternative view for universities is an active approach to the triangle human – nature – society [12]. This research aims to outline the environmental consciousness of students based on their lifestyles. According to Sophie Asmar [2], students do not fully understand the concept of sustainability. Sustainability has not been included in their core curriculum. Most of the ones that are interested have either attended courses that teach the concept of sustainability or are on their own curious to learn about this concept. Durkheim in his theory (Functionality Structural - Structural Functionalism), says that society is changing to meet the new environmental needs [4]. Sustainable education is at an early stage to be adapted by society and the educational institutions. Sustainable development is not yet a model to be replicated for universities [4].

METHODOLOGY

Raw data were collected using questionnaires. The design of the questionnaire is based on a previous research’s questionnaire, which took place in Santa Clara (USA) University [2]. Our goal was to examine whether students of Mytilene, at Lesvos Island, understand the concept of sustainability, and, if they are influenced so as to adopt sustainable lifestyle and embrace environmentally sustainable behaviors. The questionnaire was translated and adapted to Greek language, in order to enable all students to effectively respond to the questions. The questionnaire contained 13 questions, divided into four categories depending on their contents. The first category included questions on various types of sustainability. The second category included questions on environmentally sustainable behaviors. The third one questioned implementation of environmentally sustainable behaviors while the last category dealt with the importance of being part of an environmentally aware group. We also took two hypotheses. The null hypothesis, that there no connection between demographics and the environmental sensitivity of students and the alternative hypothesis that there is a connection between them. A random sample, of 300 questionnaires, was distributed to the various university departments. Fifty-one questionnaires were returned from the Department of Environment, 51from the Department of Social Anthropology and History and 51 from the Cultural Technology one. The rest of the questionnaires were returned from the Departments of Sociology, Geography and Marine Sciences, specifically a total of 49 from each of the mentioned departments. Finally, only 193 of the collected ones were suitable for statistical analysis. The total University of the Aegean population is 4000 students.

RESEARCH AND RESULTS

From the total of 193 respondents, the 23% were male and the majority (77%) female (Figure 1).

Concerning the age of the participants, most (20%) are in their 21st year of age. The ages of 20, 22 and 19 are recorded as the 18%, 18% and 17% of the sample respectively.Students of age 23 or older represent the 14% and those aged 18 comprise the 13% of the sample (Figure 2).

Regarding the year of studies, the largest percent of responses (24%) appears to be in their third year of studies, followed by first-year students, a 22.3%. The table below presents the rest of responses (Figure 3).

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The University of the Aegean at the Mytilene (Lesvos Island) campus offers 2 directions of studies, the Social Sciences and the Environmental Sciences, with 71% of students in the Social ones (Figure 4).

The respondents were quite equally distributed in the various participating departments (Figure 5).

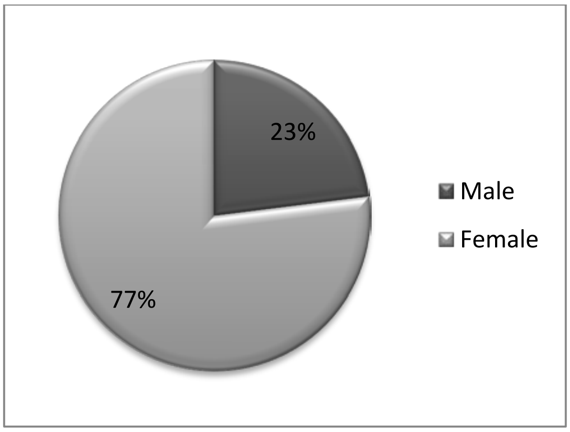


Figure 1: Responders by Gender

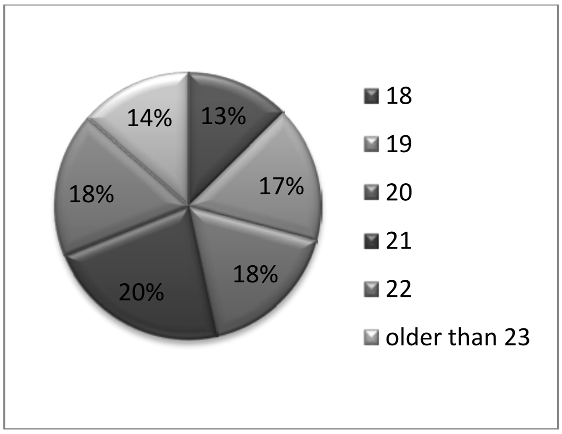


Figure 2: Responders by Age

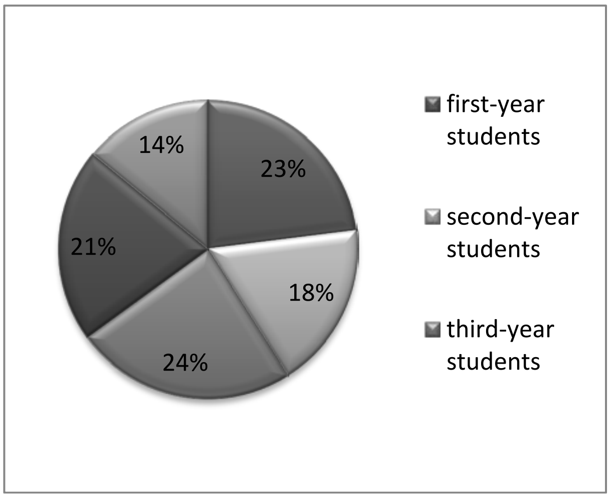


Figure 3: Responders by Class Year

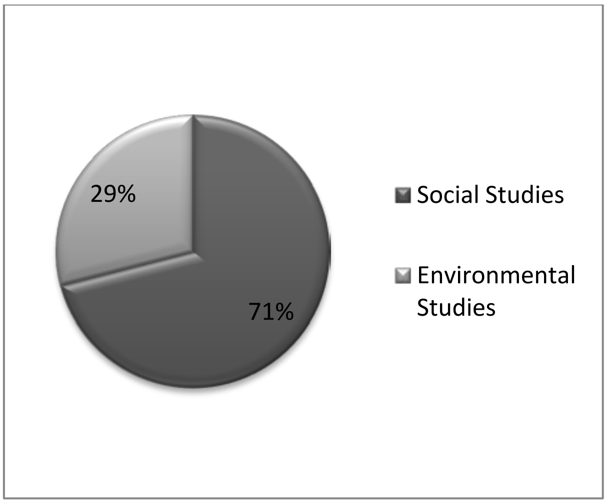


Figure 4: Responders by Directions Studies

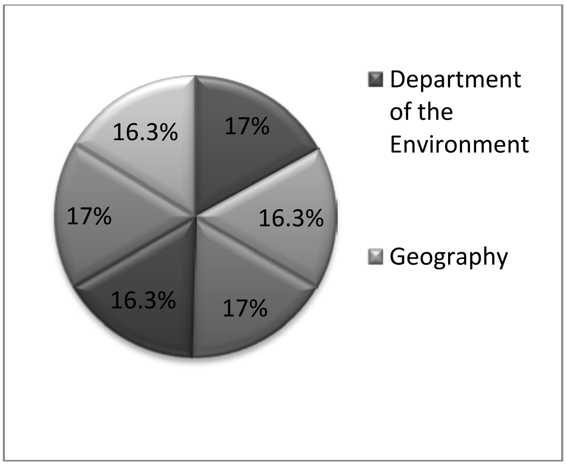


Figure 5: Responders by Department

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After the questions about demographics, are the ones about the environmental issues.The questions were divided into 4 categories. The first category concentrated on the terminology of sustainability, attempting to assess how students define sustainability. Diversity was chosen as extremely important. The terms (Figure 6) that students had to choose in relation to sustainability were:

- Diversity
- Civic Engagement
- Energy Conservation
- Economic Viability
- Nature
- Social Justice
- Long-term approach to global problems
- Climate Change
- Human Rights
- Economy
- Environment
- Social Equity
- Ethics
- Health

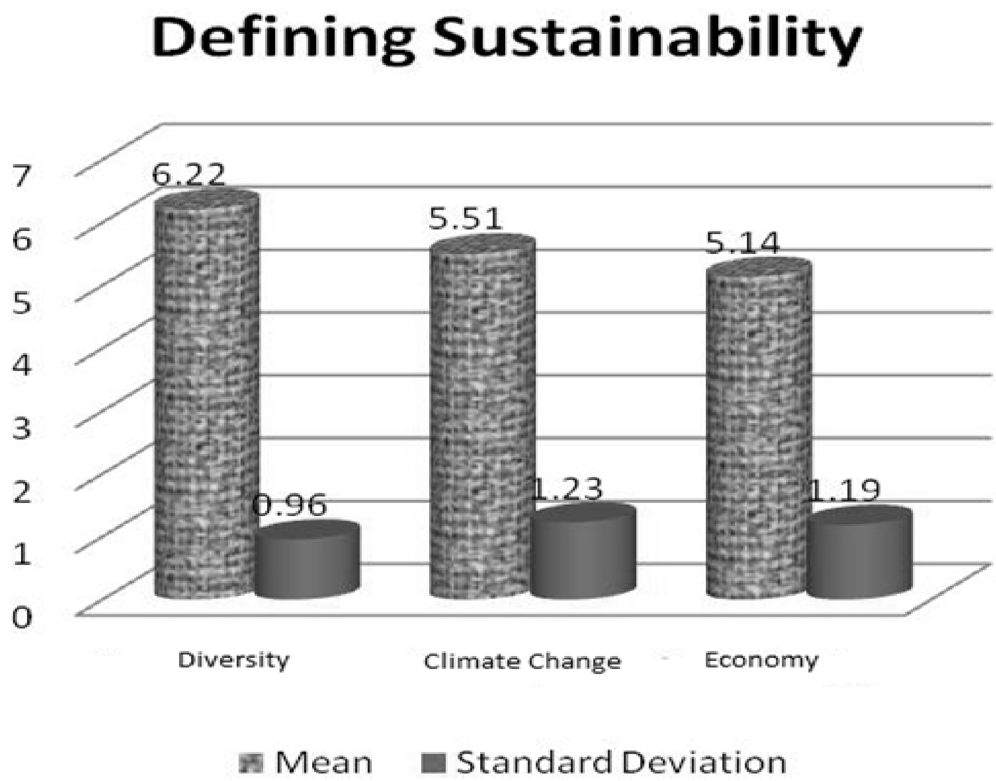


Figure 6: Defining Sustainability

The second category was composed of questions about environmental sustainable actions (Figure 7). Concerning the actions that are considered as most important for achieving the environmental sustainability the students chose between 6 different situations. The younger ages answered thatthe wise use of waterand buying energy efficient appliances(mean: 6.06, standard deviation: 1.14) were the most important ones. On the other side, women found recycling(mean: 6.23, standard deviation: 1.11) to be the most impactful actionfor the achievement of environmental sustainability. The departments in the Environmental Sciences divisionfavored using fuel efficientcars (mean: 5.94, standard deviation: 1.24). Finally they found eating less beef (mean: 4.20, standard deviation: 1.93) to be significantly less important than the rest of the actions regardless of their demographic differences.

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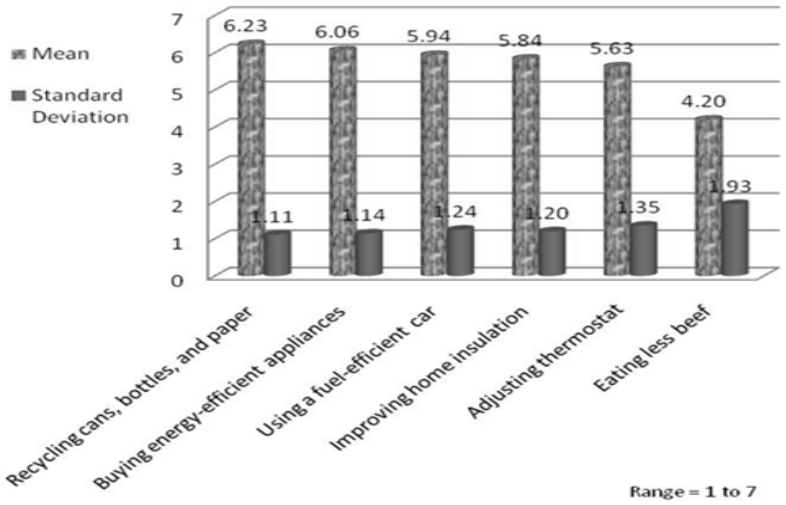


Figure 7: Situations for achieving environmental sustainability

The third category of questions focused on the reasons behind applying environmental friendly behaviors.The related statements can be seen below:

- For the pleasure I sense when I find ways to improve the quality of the environment
- Because it's the logical thing to do in order to help the environment
- Because I love the feeling when I do things for the environment
- For the pleasure I get when I do things for the environment
- Because other people will get angry if its not done
- Because I would feel ashamed if I didn't do something about the environment
- Because my friends insist in doing it
- Because being environmental friendly it's part of my identity
- Because it's part of the way I chose to live
- To avoid being criticized
- I don't know. I don't understand how my efforts, being environmentally friendly can help the situation of the environment

Women stated that it's the logical thing to do. Men supported that other people will get angry if they don't do it. Respondents from the Environmental Sciences division answered that it's their lifestyle and from the Social Sciences that they would feel ashamed if they didn't do something about the environment. Finally, in the fourth category, to the question about how important it is to participate in an environmentally active community, we accept the null hypothesis, that there is no relation between demographics and environmental awareness in students. This means that regardless of age, college year, college, department and gender, students consider that is quite important to belong to an environmentally sensitive group (Figures8-12).

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of 13 How important is it to you to feel a sense of community with other community members? is the same across categories of Gender.	Independent-Samples Mann-Whitney U Test	.092	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Figure 8: Hypothesis test summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of 13 How important is it to you to feel a sense of community with other community members? is the same across categories of College.	Independent-Samples Mann-Whitney U Test	.246	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Figure 9: Hypothesis test summary

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	Null Hypothesis	Test	Sig.	Decision
1	The distribution of 13 How important is it to you to feel a sense of community with other community members? is the same across categories of Department.	Independent-Samples Kruskal-Wallis Test	.640	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Figure 10: Hypothesis test summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of 13 How important is it to you to feel a sense of community with other community members? is the same across categories of CollegeYr.	Independent-Samples Kruskal-Wallis Test	.892	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Figure 11: Hypothesis test summary

	Null Hypothesis	Test	Sig.	Decision
1	The distribution of 13 How important is it to you to feel a sense of community with other community members? is the same across categories of Age.	Independent-Samples Kruskal-Wallis Test	.933	Retain the null hypothesis.

Asymptotic significances are displayed. The significance level is .05.

Figure 12: Hypothesis test summary

4. DISCUSSION AND CONCLUSIONS

In conclusion, for questions concerning the awareness towards the environment and the ways in which participants pursue their sustainable behavior, age plays an important role, since the students between 20-23 years seem quite savvy about the environment. At the same time, sex shows to affect the given answers, with women being more sensitive about the environmental issues. There is a need to explore, in more detail, the potential of gender in the context of environmentally responsible behavior, as literature research reports that women show stronger environmental concern and attitudes than men. Perhaps when environmental educators fully take on board the need for a gender dimension in environmental education programs, will students be equipped to envision a more sustainable society [13]. Irrelevant of the year of their study, there was a consistent environmental awareness. Regarding questions about the university community of Mytilene, their department, year of study and direction of study, all appear to be quite important in relation to their environmental participation.

It is also observed that students of environmental sciences are more sensitive to environmental issues than those from the social ones. This is probably due to the fact that courses and activities that promote responsible environmental behavior are priorities in the divisions of Environment Sciences curricula. Regarding the students in the Social Sciences division, as they are anthropocentric sciences, the environmental issues are lagging behind in their curricula. However nowadays, where science and technology are rapidly evolving, all students regardless of the school in which they are enrolled, must have the necessary knowledge regarding environmental issues in order to become environmentally active participants in the decision making processes. It should be stressed that knowledge of and positive attitudes toward the environment are necessary keys for making informed decisions about environmental issues [14] Environmental education has been easily incorporated into hands-on experiences, since those are the starting point of all learning [14]. Environmental education provided children with the opportunity to practice responsible environmental actions, which helped them to develop new environmental behaviors. [14].

To sum up environmental sensitivity is obviously a measurable and significant educational approach for college students in Mytilene. The is no doubt that the economic crisis during the last 6

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years has prevented students from thinking further if they have to be more sensitive against environment, because they are obligate to fulfill other important needs. Youth must be educated in and out universities in how to take care, respect and protect the environment. Environmental sensitivity must be a priority in university system's educational agenda [14]. Mytilene has two unique departments all around Greece, concerning the environment. It is necessary to promote and protect the environmental sensitivity of students studying the science of the environment. Students by all available means, must learn to care for the planet, make efforts to improve the environment and be part of an environmentally active community [14]. The study of environment is the process that will give all participants the necessary survival skills. Each one of us has to make a sincere effort to secure the quality of human life.

References

[1] Larran M., Jorge, Jesús Herrera Madueno, María Yolanda, Calzado Cejas, Francisco Javier Andrades Pena, 2015. An approach to the implementation of sustainability practices in Spanish universities. *Journal of Cleaner Production*, **106**, 33-34.

[2] Sophie A., 2009. *Culture of Sustainability: Measuring Sustainable Lifestyles at the College Level*.

[3] Steiner G., Posch Al., 2006. Higher education for sustainability by means of transdisciplinary case studies: an innovative approach for solving complex, real-world problems. *Journal of Cleaner Production*, **14(9-11)**, 877-890.

[4] Habib M. Alshuwaikhat Ismaila Abubakar, 2008. An integrated approach to achieving campus sustainability: assessment of the current campus environmental management practices. *Journal of Cleaner Production*, **16(16),** 1777-1785.

[5] Zilahy, G., Huisingh, D., 2009. The roles of academia in Regional Sustainability Initiatives. *Journal of Cleaner Production*, **17**, 1058 – 1060.

[6] Simkins G, Nolan A., 2004. Environmental management system in universities. Occasional paper for the environmental association for universities and colleges (EAUC);

[7] The University and the Community. *Creating a sustainable future through civic engagement, impact of the university of Minnesota regional sustainable development partnerships*. University of Minnesota; 1998–2006.

[8] Lozano R., Lukman R., Lozano F., Huisingh D., Lambrechts W., 2013. Declarations for sustainability in higher education: becoming better leaders, through addressing the university system. *Journal of Cleaner Production*, **48**, 10-19.

[9] Lehmann M., Christensen P., Thrane M., Tine Herreborg Jørgensen, 2009. University engagement and regional sustainability initiatives: some Danish experiences. *Journal of Cleaner Production*, **17(12)**, 1067-1074.

[10] Zimmer M.R., Stafford T.F., Stafford M.R., 1994. Green issues: dimensions of environmental concern. *J. Business Res*., **30(1)** , 63–74.

[11] Ferrer-Balas D., Buckland H., De Mingo M., 2009. Explorations on the University's role in society for sustainable development through a systems transition approach. Case-study of the Technical University of Catalonia (UPC). *Journal of Cleaner Production*, **17(12)**, 1075-1085

[12] Lukman R., Krajnc D., Glavic P., 2009. Fostering collaboration between universities regarding regional sustainability initiatives – the University of Maribor. *Journal of Cleaner Production*, **17(12)**, 1143-1153

[13] Sakellari M., Skanavis C., 2013. Environmental Behavior and Gender: An Emerging Area of Concern for Environmental Education Research. *Environmental Education and Communication*, **12(2)**, 77-87.

[14] Plaka V., Skanavis C., 2016. The feasibility of school gardens as an educational approach in Greece : a survey of Greek schools. *International Journal of Innovation and Sustainable Development*, **10(2)**, 141-159.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
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The environmental impacts of the refugees' settlements at Lesvos Island

C. Skanavis, A. Kounani*

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
* Corresponding author: Email: kounani@env.aegean.gr

Abstract

The last few years, Greece is experiencing a big economic crisis and the impacts of a refugee crisis too. Since March 2011, when the Syrian uprising turned into civil war, the intense exodus of civilians to neighboring countries made its strong appearance in the Aegean Sea, and especially at Lesvos Island in Greece. Refugee movements in such high numbers tend to produce uncontrolled, daily interruptions to the receiving region's local community environmental management. This research is trying to assess the environmental impact of the refugees at the island of Lesvos. Moreover, it is addressing the environmental footprint the island of Lesvos is up to experience, due to lack of appropriate planning and anticipation for such a huge increase of mass arrival, who desperately try to find shelter and assistance before (and if) they ever continue their journey to other European countries.

Keywords: refugees; Lesvos Island; environmental footprint; environmental impact; Greece

1. INTRODUCTION

Due to wars, conflicts, natural disasters and environmental accidents [20], mass refugee movements have occurred. People with low resiliency are enforced to relocate [7], on their desperation to find a safer place to go on with their lives. World history proves that the most dramatic migration movements were: firstly, the one of 12 million Germans migrating from Eastern Europe to Western Europe after the Second World War [2] and secondly, the one caused by the Syrian war. Syria is presenting the biggest humanitarian and refugee crisis of recent years, a continuing cause of suffering for millions of people [31].

Globally, by the end of 2014, almost 60 million people were forced to leave their homes due to the war, discrimination or violation of the human rights. This mass exodus of people from their own country has exponentially increased in our days. The consequences of this global phenomenon are much bigger than the actual issue itself. Whenever refugees settle in a specific area, it is mathematically proven that they will affect the social, environmental and political environment of the hosting region [12]. Due to lack of appropriate planning and anticipation for such an intense increase of people arriving, especially when the hosting nation does not have sustainable and integrated management plans, regarding the above mentioned concerns, the problems that are caused are unaffordable [11].

1.1 Environmental degradation caused by refugees

Obviously emergency conditions, such as the sudden appearance of a large number of refugees, have a major impact and pressure on the environment of the receiving area. Nobody expects refugees to be environmentally conscious while they are fighting for their lives and crossing hundreds of miles daily to find a better life for them and their children. Refugees' mentality,

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behavior and overall awareness on the importance of environmental issues have to be analyzed from different points of view than what we are accustomed to [16]. Hence, the issues of concern should be assessed from the host's point of view. To name some of the host country's focal points: improved sanitary and waste systems in refugee camps, upgraded waste management on the entering location, increased international assistance to arriving refugees. Obviously, a waste management scenario that is characterized by low collection capacity, low manpower, lack of recycling sorting system, poor treatment technology and uncontrolled landfills could lead to environmental and humanitarian hazards [6,9]. The arrival of refugees is resulting to further land degradation and increased waste production. Failure to mitigate these impacts, would lead to environmental pollution [11], which will directly affect human's health. Another consequence is the burden of diseases, which do not only jeopardize the health status of refugees but of the hosting communities as well [21].

The management of solid waste is an important concern in emergency conditions, e.g. those of a refugee camp [5]. Improper waste management activities can: a) increase disease transmission or otherwise threaten public health, b) contaminate ground and surface water (solid waste streams can disperse toxic materials and pathogenic organisms into the leachate of dumps and landfills), c) create greenhouse gas emissions and other air pollutants. Public health and hygienic standards are considered very important aspects to safeguard quality of health, placing therefore the waste management as a top priority [11].

This paper will give an overview of the Syrian refugee situation and the resulting environmental consequences at the island of Lesvos, in Greece, which happens to be a major entry point on European Land. This research will therefore try to assess the refugees' ecological footprint at Lesvos Island.

1.2 The Syrian war – The refugee crisis

The Syrian civil war started in spring 2011, well known as Arab Spring. Pro-democracy protests, all-over the country, stood against President Bashar Al Assad's, who was characterized by authoritarianism, political corruption and human rights violation. Protesters were armed with the help of opposition militias who have been fighting against governmental forces. At 2012 the conflict has erupted in full-grown civil war between the pro government ones against the ones opposing to it [8]. At the same time, it is a religious war between different ethnic groups in the Arabian world [2]. This war is ongoing and causes massive migration of people from Syria and the surrounding countries as well to Europe [22].

By the time Syrian war has started, as the United Nations High Commissioner for Refugees (UNHCR) announced in 15th of March 2016, from a total population of 20 million, more than 470000 people have been killed, 4.8 million have fled the country and 6.6 million have been displaced inside Syria [31]. A majority of refugees have fled to Jordan and Lebanon [15], straining the already weak infrastructures and limited resources there. According to UNHCR [29] sources, 4834880 refugees from Syria have been registered elsewhere until 5th May 2016, with 95% of them found in five countries: Turkey, Lebanon, Jordan, Iraq and Egypt [1]. Specifically, 2.1 million Syrians were registered by UNHCR in Egypt, Iraq, Jordan and Lebanon; 1.9 million in Turkey, and more than 26700 refugees in North Africa. More than two million Syrians, along with migrants and refugees from other war-torn countries, have fled to Turkey and attempted to cross Mediterranean Sea (Figure. 1) to seek refuge in Europe, overwhelming receiving countries, since they weren't ready or willing to cope with this sudden outcome [31].

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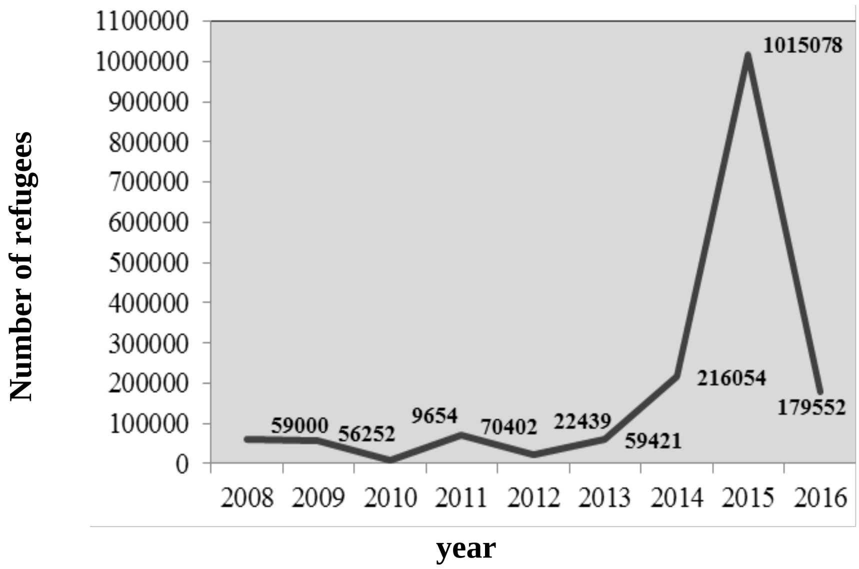


Figure 1. Sea arrivals to Mediterranean Sea from the year 2008-2016 (based on data received in 16th April 2016 by UNHCR)

1.3 The refugee crisis and the Greek involvement

This massive immigration is known as the "Middle East Refugee Crisis", and obviously it has affected all the neighboring to Syria, countries including Greece. The UN Refugee Agency announced in 16th of March 2016, that more than one million people, mostly refugees from Syria, Iraq and Afghanistan, have crossed into Greece since the beginning of 2015 [33]. UNHCR has pointed out that up to 14th March 2016 more than 143634 refugees have arrived to Greece from Turkey, bringing the total number of such arrivals into Greece to 1000357 since the January of 2015. So far 448 people have drowned or are missing compared to a total of 3771 for last year [33]. UNHCR has reported that more than one million refugees reached Europe last year, including the arrivals from Libya to Italy [33]. Figure 2 shows the countries receiving the majority of the refuge movement for the year 2016.

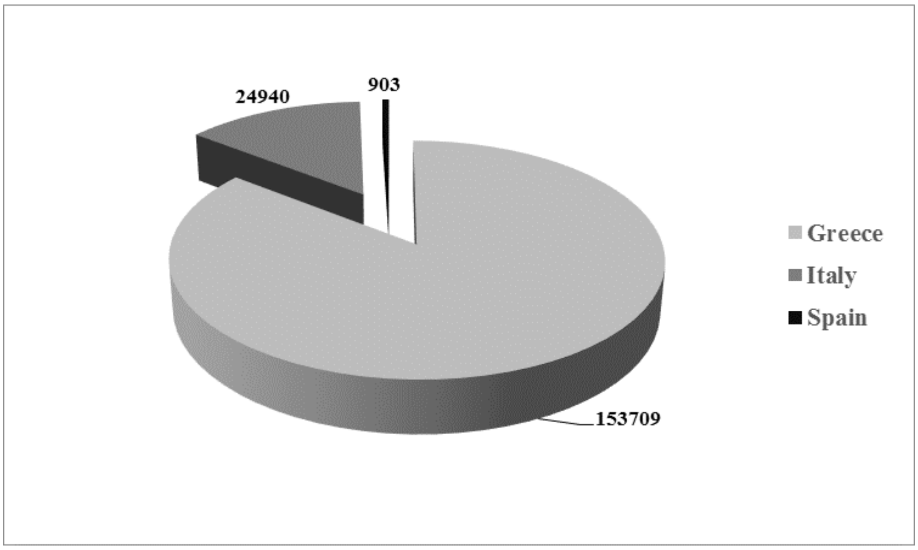


Figure 2. Refugee Crossing the Mediterranean Sea per receiving country for the year of 2016 (based on data received in 16th April 2016 by UNHCR)

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For more than seven years refugees and migrants from Syria, Afghanistan and Iraq have been crossing Mediterranean Sea heading to Greece [28]. However, Greece is not their final European destination since they wish to continue their journey to northern and western EU countries. All these years, Greek islands, like Lesvos Island, are facing an enormous pressure to deal with such large number of refugee arrivals [29].

The islands that are near Turkey, such as Lesvos, Kos, Chios and Samos (Figure 3) happen to have limited economic resources and a fragile environmental sustainability structure making them very fragile in emergency situations, like the one related to the Middle East Refugee Crisis.

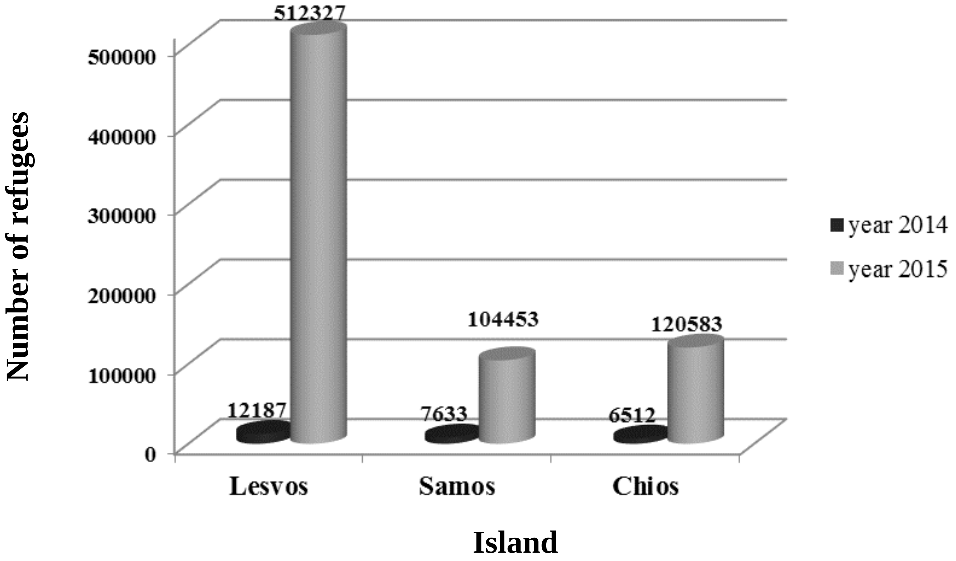


Figure 3. Number of refugees that reach the Greek Island, the years 2014 and 2015 (based on data received in 16th April 2016 by Hellenic Police) [23].

Greece the last decade has been seriously affected by the global economic turmoil [13]. This crisis has caused a dramatic impact on everyday life, since the reduction or absence of income caused losses in prosperity and pushed large sections of the population in poverty [14]. The national health system has been in jeopardy, which makes even harder the delivery of services to the latest refugee flow.

2. CASE STUDY

2.1 Refugees and Lesvos Island

The island of Lesvos is located in the North-Eastern Aegean Sea, in Asia Minor, and with an area of 1636 km^2, is the third largest Greek island after Crete and Evia. It has a coastline of 370 km.

The Municipality of the island of Lesvos consists of 13 sections and 190 villages with a total population of 86436 residents. Based on census data for the years from 1981-2011 for the island of Lesvos, a population decrease is observed (Table 1).

The main island activities include farming, fishing and agriculture. Lesvos Island is well known for its local products (olive oil, ouzo, honey, wine and cheese) [19]. In 1987, tourism as a well-defined business investment makes its appearance and has been growing steadily since then [4]. With its beautiful, unique and full of variety landscapes, the island has developed ecotourism and other forms of alternative tourism investments.

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Table 1. Population flow on the Lesvos Island (Data from the Greek Statistic Services)

Year	Population	Growth rate
1981	108840	
1991	90790	- 16,6%
2001	94283	+ 3,8%
2011	85330	- 9,5%

Consequently, this concept attracts many tourists with different expectations and interests. Lesvos has a significant number of hotels operating which provide over 6000 beds and another 7500 ones through rentals [25]. The total number of tourists, who visited the island, in 2015, was around 168721, which is twice the number of the island's residents. Nevertheless, a slight decrease in tourism flow, probably related to the refugee concept, has made its appearance, seriously puzzling the local community who fears further reductions in one of their vital investment sectors.

2.2 Municipal solid waste (MSW) production and environmental management of Lesvos Island

According to receiving data from the "Service of Planning Department, Cleanliness, Recycling, Waste Collection" of the Municipality of Lesvos the amount of MSW on the island is about 100 tones / day in winter and ranges from 120-130 tones / day in the tourist season. Specifically, in 2014 the amount of unsorted waste was 37146 tones plus the waste in recycle bins, which came up to 1285 tones, thus the total quantity of waste was 38331 tones. The unsorted wastes were collected from about 8000 bins and the recyclable ones from approximately 1600 blue bins. The wastes' collection is done, by the 40 vehicles for the unsorted ones and by 4 vehicles for recyclable materials. The vehicles making careful arrangements and several trips each manage to cover a significant portion of the whole island's needs. The Central Sanitary Landfill Disposal of the island has 307 acres of land. The responsibility of uploading, disposal and recovery of wastes is placed on the Municipal Waste Management and Environmental Development Company of Lesvos. Sorting, compression, and sale of recyclables is occurred in a private center, the Recycling Sorting in Moria area, run by the company "Sea-Lesvos Foundries Recycling SA" [3].

2.3 Environmental degradation before the refugees' mass movements

The most important part of the production of solid waste on Lesvos is from tourism related activities (restaurants, hotels etc.) during the summer season, which officially starts on the 15th of May and ends on 15th of October, with peak period from 15th of July until 15th of August. According to the waste amount and type, waste producers on Lesvos Island, can be divided into: residents of urban areas, residents of rural areas, international tourists and Greek tourists. The amount of waste is increasing and the composition is changing. Especially the seasonal tourist population affects the island's basic infrastructure. Traveling to the main landfill is too long to make it economically feasible for daily transfers and therefore transportation of waste happens sporadically. Other than that, waste of illegal immigrants is the main cause of beach litter in Lesvos [10], which along with tourists' waste are the main sources of such pollution.

In Lesvos most of the large hotels and almost all the hotels located in remote areas have biological wastewater treatment plants, as required by the Greek government [18]. The treated water is recycled through irrigation of hydrophilic plants or disposed to the environment after taking the necessary permits. Most of the biological wastewater treatment plants of the hotels are not operating satisfactorily. They especially face problems due to the seasonality. The flow reduction in the low season jeopardizes biomass's re-activation. Lack of experienced personnel is another problem.

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Many of the sewage systems are under construction [18]. By 2018 all wastewater must have been treated before its discharge [17]. By then, 36 wastewater treatment facilities should be operational. Twenty-six of them will include secondary treatment and disinfection, making treated water appropriate for irrigation purposes. In addition to this, industry wastewater produced by ouzo distilleries, slaughterhouses, cheese and dairy industry and, most importantly, olive oil mills has major impact on the environment. Especially the olive oil industry since its sewage is quite polluted and difficult to be treated [18].

2.4 Environmental degradation after the refugees' mass movements

The majority of refugees were staying at Lesvos for 2 – 4 days, for registration purposes. Then they were being transferred to Athens in order to continue their journey to Northern European countries. Recently due to the closure of European borders a significant number of them has been trapped to Lesvos Island with ambiguous departure date.

The major waste problem Greek island face, due to refugees' movement is the disposal of plastic from their life jackets and inflatable crafts, which remains behind upon their arrival to the islands. Plans by several Ministries have been proposed in order to deal with the issue. Moreover, landfill capacity is not adequate for the unexpected inflow of people in the islands where refugees arrive. The volume of lifejackets collected until April 2016 was 16000 cubic meters. This type of waste has been collected and transferred to 3 municipal stations, in an effort to find a way to recycle it. The materials though, the life jackets are made from, cannot be recycled in Greece.

Regarding the production of Municipal Solid Waste, the Municipality of Lesvos while trying to assess the amount of pressure the island is up to, due to the number of refugees that are hosted at the island daily (including the hosted NGO members, journalists, etc.) carried a study. Based on this study, it was concluded that the daily production of MSW related to the refugees' flow ranges between 7 to 30 tons, with a daily cost for collection - transport – landfill services, between 1500 to 5500 euros. In this amount it is not included the cost for 'special' waste cranes - trucks etc., cleaning of affected beaches, cleaning of areas where refugees stay, and cleaning of the port that occasionally gets occupied [3].

Some refugees are staying at the camps and some of them at hotels and apartments. Several camps do not have wastewater purification system for waters from showers and kitchens, but are only equipped with toilet toi-toi system which is again transported to the waste pit of septic tanks and to the pine forest "Tsamliki" where all the residues of the water treatment facilities in Lesvos are being discharged. NGO representatives dealing with the refugee crises have been using rental cars and there is also an increased demand for public busses operation. This automobile use increase adds to existing air pollution problems due to excess emissions.

3. DISCUSSION AND CONCLUSION

Contemporary life activities exert intense pressure on nature and result in some kind of environmental degradation. In the recent refugee inflow scenario, in Lesvos Island, the evaluation of the emerging environmental concerns bring to light the lack of a state of art environmental management system to start with.

The refugees' footprint can be summarized as: pressure on water and energy demand, soil destruction, air pollution, deforestation, waste production. However, every refugee crisis is unique and needs to be observed and managed as an individual condition [26]. In the case of Lesvos, refugees were staying a maximum of 14 days before they continued their journey towards northern and western EU countries. Now this has changed, because refugees have been trapped in the island, since the European borders have been closed. The biggest impact refugees have on waste production is because of their safety equipment: lifejackets, inflatable boats and belts. When it

comes to solid waste, there is a large increase because of them staying for days into camps. Therefore, overpopulation of Lesvos Island is projected that it could cause significant environmental degradation. Greece was not well prepared to deal with the refugee flow while being also in a harsh economic crisis situation.

And while some businesses are making a profit from the refugees' stay at the island, the long term prosperity of the island's economy and environment need to be studied in great detail.

Acknowledgments

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References

[1] Amnesty International, 2015. Syria's refugee crisis in numbers. Available at: https://www.amnesty.org/en/latest/news/2015/09/syrias-refugee-crisis-in-numbers/

[2] Bahcekapili C. and Cetin B., 2015. The Impacts of Forced Migration on Regional Economies: The Case of Syrian Refugees in Turkey. *International Business Research*; **8**(9), 1-15 (DOI: http://dx.doi.org/10.5539/ibr.v8n9p1)

[3] Bletsa G., 2014. The Organization and Operation of Collection & Transfer Solid, Non Hazardous waste of Municipality of Lesvos. Research of the Service of Cleaning and Recycling of Lesvos Island, Lesvos

[4] Camatsos C. and Backman M., 2009. Tourism in Lesvos, Greece. Available at: file:///D:/Downloads/presentation%20C2CI%20Lund%20%20Tourism%20in%20lesvos.pdf

[5] Collivignarelli C., Sorlini S., Vaccari M., 2004. Solid Wastes Management in Developing Countries. *CD-ROM Proceedings of ISWA 2004 World Congress*, October 17–21, Rome, Italy.

[6] Garfi' M. and Bonoli, A., 2009. Waste disposal in Development Countries and emergency situations. The case of Saharawi refugee's camps. *International Solid Waste Association (ISWA) World Congress 2009*, Lisboa, Portugal.

[7] Giannoulis C., Skanavis C., Karapatsiou E., 2014. Environmental Awareness: Environmental Accidents as an Example to be Avoided. A Summative International Analysis Studies in Media and Communication, *Published by Redfame Publishing*, **2(1)**, 38-48

[8] Holliday, J. 2013. The Assad Regime: From Counterinsurgency to civil war. *MIDDLE EAST SECURITY REPORT 8. Institute for the Study of War*, Washington, 42 Available at: http://www.understandingwar.org/sites/default/files/TheAssadRegime-web.pdf [Accessed: 25th February 2016]

[9] Hoornweg, D. and Bhada-Tata P. 2012. What a Waste: A Global Review of Solid Waste Management. *Urban Development and Local Government Unit, World Bank.*

[10] Katsanevakis S., 2015. Illegal immigration in the eastern Aegean Sea: a new source of marine litter, *Medit. Mar. Sci.*, 16/3, 605-608

[11] Kherfan R. A., 2016, What are the most pressing environmental concerns of refugee camps in conflict-zones?, *American University of Beirut, Faculty of Health Sciences, Department of Environmental Health*, p.14, (DOI: 10.13140/RG.2.1.3245.4162)

[12] Kreibaum, M., 2016. Their Suffering, Our Burden? How Congolese Refugees Affect the Ugandan Population, *World Development*, **78**, 262–287

[13] Kentikelenis, A., Karanikolos, M., Papanicolas, I., Basu, S., McKee, M., Stuckler, D., 2011, Health effects of financial crisis: omens of a Greek tragedy, *The Lancet*, **378 (9801),** 1457–1458, 22 October 2011, DOI: http://dx.doi.org/10.1016/S0140-6736(11)61556-0

[14] Knight, D. M., 2013, The Greek economic crisis as trope, Berghahn Journals Focaal, Volume 2013, Number 65, Spring 2013, pp. 147-159(13)

[15] Refaat, M.M., Mohanna K., 2013. Syrian refugees in Lebanon: facts and solutions. *The Lancet*, **382 (9894)**, 763–764.

[16] Oakes, R. P. 2007. Desert Trash: Illegal Immigrants' Impact on the Environment, Available at: http://www.nyu.edu/classes/keefer/EvergreenEnergy/oakesr.html [Accessed: 8th December 2015]

[17] Paraskevas P.A. and Nikolakopoulos G.N., 2011. Treated Waste water reuse in the water management plan of Lesvos Island, Greece. *Proceedings of the 12th international conference on environmental science and Technology*, Rhodes, Greece. 854, Available at: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=15346 [Accessed: 22th February 2016].

[18] Paraskevas P.A., Giokas D.L., Kolokythas G. Haralampopoulos, D. Stathelli, A., 2001. Waste water management in the island of Lesvos, Greece. *7th International Conference on Environmental Science and Technology Ermoupolis, Syros island, Greece* – Sept. 2001, 396 – 402.

[19] Rontos K. Kitrinou, E. Lagos D., Diakomihalis M., 2012. Islands and Tourism Development: A Viewpoint of Tourism Stakeholders of Lesvos Island. *In: Business, Management and Economics "Visions for Global Tourism Industry - Creating and Sustaining Competitive Strategies"*, 461 – 480.

[20] Sakellari M. and Skanavis C., 2012. An overview of the climate refugees' issues and scenario, *Chapter In book: English through Climate Change*, Publisher: Department of Forestry and Management of the Environment and Natural Resources, Democritus University of Thrace, 127 – 139

[21] Stich A., 2015. Coming in to the cold – Access to health care is urgently needed for Syrian refugees. *Travel Medicine and Infectious Disease*, **13 (6),** 445–446.

[22] The Lancet, 2014. The war on Syrian civilians. *The Lancet Editorial*, **383 (9915)**, 383

[23] http://www.astynomia.gr/images/stories//2016/statistics16

[24] European commission, 2014. A Common European Asylum System. Luxembourg,

[25] Regional Tourism Organization Mytilene, Lesvos, January 2016. Telephone interview with representative of Regional Tourism Organization Mytilene.

[26] UNHCR, 2011. "Convention and Protocol Relating to the Status of Refugees". Published by: UNHCR, Communications and Public Information Service, P.O. Box 2500 1211, Geneva, Switzerland.

[27] UNHCR, 2015. Europe is living through a maritime refugee crisis. The sea route to Europe: The Mediterranean passage in the age of refugees.

[28] UNHCR, 2016a. What is a refugee? Available at: http://www.unrefugees.org/what-is-a-refugee/ [Accessed: 11th February].

[29] UNHCR, 2016b. Syria Regional Refugee Response. Inter-agency Information Sharing Portal. Source - UNHCR, Government of Turkey. Available at: http://data.unhcr.org/syrianrefugees/regional.php [Accessed: 5th May 2016]

[30] UNHCR, 2016c. Working with the European Union. Available at: http://www.unhcr.org/pages/4dd12ad46.html [Accessed: 24th February 2016].

[31] UNHCR, 2016d, "Syria conflict at five years", Available at: http://www.unhcr.org/56e6e1b991.html [Accessed: 15 March 2016].

[32] http://data.unhcr.org/mediterranean/regional.php

[33] UNHCR, 2016e. More than one million refugees travel to Greece since 2015. Available at: http://www.unhcr.org/56e9821b6.html[Accessed: 16th March 2016]

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Literature and environmental education: The case of Alexandros Papadiamantis

E. Manolas[*], G. Tsantopoulos

Department of Forestry and Management of the Environment and Natural Resources,
School of Agricultural and Forestry Sciences, Democritus University of Thrace,
193 Pantazidou Street, 68200 Orestiada, Greece.
*Corresponding author: Email: emanolas@fmenr.duth.gr

Abstract

Today the need for creating an environmentally sensitive citizenry is perhaps greater than ever. Literature is one of the ways in achieving such a goal. In this paper the achievement of such a goal is attempted through the use of short stories and, in particular, though the work of Alexandros Papadiamantis, one of the most skilled short story writers of modern Greece. First, this paper offers a discussion of the importance of literature, and in particular short stories, for environmental education. Second, after listing some of Papadiamantis' most ecologically oriented short stories the paper discusses the importance of nature in the writer's work. Third, this article offers suggestions of active learning activities which can help students explore the values they hold and open a fruitful environmental dialogue.

Keywords: literature; environmental education; Alexandros Papadiamantis.

1. INTRODUCTION

In the field of education, literature can be useful for aesthetic quality, for cultivating emotion, for language development and for the knowledge it offers. It can also be useful as a prevention mechanism for undesirable situations as well as provide solutions [1].

Literature can help in shaping positive attitudes and activating learners towards a multiplicity of problems including the environment. Literature can also contribute to the transmission of values and ideologies depending on the text studied [2].

People accept information more easily when their mental defences are not activated and so fiction may be a more effective learning tool than a factual text [3,4]. Also, through fiction audiences can be "transported" into the story and take the relevant information back to real life [5]. Also, the heroes of stories can set examples for students to follow or avoid. In addition, it can help them build their own attitudes and views through analyzing their own behaviour towards others, the environment or life in general [6].

Among Greek writers who praise nature Alexandros Papadiamantis (1851-1911) would certainly be the first to mention. In many of his texts he reveals the greatness of nature and the interdependence of man and nature [7].

Short stories are among the most suitable literary tools for teaching purposes since: a) they are practical as their length is long enough to cover entirely in one or two class sessions, b) they are relatively easy for students to work with by themselves, c) they have a variety of choice for different preferences, and d) they can be used with all levels, all ages and all classes [8].

This paper, through Papadiamantis' most ecologically oriented short stories, discusses the importance of nature in the writer's work. As "this type of literature…reveals the unity and

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importance of the coexistence of all species, it reveals the magic of nature which renews, which gives rebirth, which is the core of ecological consciousness" [9] such literature can help in the formation of attitudes and behaviours towards the environment [7]. The paper finally puts forward some ideas for discussions, debates or essays which can contribute to shaping attitudes, views and behaviours.

2. PAPADIAMANTIS AND NATURAL ENVIRONMENT

"Trees have soul, branches ache when broken, yet they please with their perfume and shadow those who hold them. They prevent bad things from happening, they are used for medical purposes, and they calm the soul!" [10]

In the majority of his stories Papadiamantis frequently refers to the gullies, the ravines and the high grounds of his home island Skiathos. He also refers to the island's little harbours, cliffs, caves, seashores. His unforgettable child memories dominate Papadiamantis' writings. He turns his memories into stories enriched with his religious experiences, or the troubles and the joys of the poor people of his island. In addition to his child memories he also derived the subjects of his stories from the poor neighborhoods of Athens [11].

Papadiamantis has defined the substance of his work this way: "Regarding myself, as long as I live, as long as I breathe and have my senses, I shall not stop praising my Christ with adoration, describe nature lovingly, and paint with affection the true Greek ways of living" [11].

Nature is the protagonist in many of Papadiamantis' short stories. Some examples: "Around the Lake", "The Crucible", "Under the Royal Oak Tree", "The Dead Traveller", "The Black-Scarved Woman", "Dream on the Waves", "Theros-Eros". His most ecologically oriented stories are: "Under the Royal Oak Tree" and "Dream on the Waves".

Papadiamantis' writings cover all types of plants: brambles, maidenhairs asparagus, myrtles, honeysuckles camomiles, wild olive trees, pomegranate trees, almond trees, oak trees, chestnut trees… [12]

Papadiamantis' writings contain plenty of ecological-nature loving content without the scaremongering we would most likely find in today's environmentally oriented fiction. His work records the inner world of a person in love with nature but at same time his stories deal with nature fully and deeply. This quote reveals the above points well: "Environment in its full definition, as horizon and base, as perspective, as substance and phenomenon, as language, as man, as society, as world and nature, as matter and God, as life and death, that is the whole exists everywhere and described and analyzed directly and indirectly…" [13]

His short story "Under the Royal Oak Tree", which is widely regarded as his most ecologically oriented short story, reveals the impact of an oak tree on the soul of the author. In this oak tree lives the muse Amadrias who enchants him and calls him as a living creature would do. The calling comes from a dream. The story conveys many messages and can attract the attention of the most indifferent youngster:

"I was so moved to look at this magnificent tree…Its branches, its berries, its leaves, seemed in the blow of the wind to sing the psalm…" Papadiamantis' description is superb. The strength of the images he conveys is overwhelming. The story is of particular importance to those who live in urban centers, who are deprived of a relationship with nature. He provides small journeys in the great paths of nature. The love the child feels for the royal oak – beyond the dream and the mirage – expresses the primary relationship of the people of this land with nature which, according to Elytis, "…constitutes neither past, nor present, nor future, it constitutes an impression, in a given historical moment and on specific material, of an unchanging expressiveness which has always characterized every Greek and is always the same" [7].

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The world and the creation are very clear in Papadiamantis' mind. For Papadiamantis, paradise is the world of God, for this is what he always wanted. His relationship with beauty is characterized by directness; he is not dependent on sterile romanticisms…or "worship the creation without God's guidance" [14].

For Papadiamantis

> nature is an inseparable part of God's creation and apocalypse, which gradually unfolds itself in a collage of everyday occurrences. Through the interchange of these images from his physical environment, the writer re-establishes the symmetry and harmony of all things, including eros, whose strength is paralleled with the strength of the embodied natural elements. Eros and nature define mystically the existence of the young and without problems shepherd, in the short story "Dream on the waves", whose ontological self-sufficiency is consciously completed through the ecstatic but simultaneously two-way relationship-coexistence he has with nature [12].

The description of nature reveals the lyricism of the writer, since through the use of simple elements – rocks, caves, waves – he paints a picture of outstanding beauty. The basic images which synthesize this landscape-seascape are: a) the lyrical image of the seashore which makes nature seem alive and indeed with magical powers. Man and nature coexist in harmony, they are one. b) The image of the sunset creates a sense of eroticism and reinforces the magical effect of nature on man, c) The whole area acquires through Papadiamantis' lyrical description a magical and divine dimension and is the place the central episode of the story will take place. The detailed description of nature reveals the magical effect of nature on man but, also, it reveals the happiness which is created by man's contact with nature.

The text reveals the writer's love for nature. For the writer man is happy only when he is close to nature. Beauty, happiness and innocence originate from her as opposed to the decay and unhappiness man feels when he is away from nature. The text reveals the writer's repugnance for the way people live in urban centers and his nostalgia for living close to nature [15,16].

In the "Dream on the Waves" the protagonist is an unhappy and oppressed person, a lawyer doing his apprenticeship. In order to find happiness and freedom the protagonist goes back to his puberty. Such a memory is the central theme of the story. The narration is done in first person and the writer seems to claim that he heard and copied this experience from someone else. Thus, the reader is given the opportunity to see things through the eyes of the narrator-protagonist and, therefore, experience the same feelings.

The author uses in the story real names of places in the island which he describes with full detail as well as similes which define the characteristics of landscapes-seascapes. These elements hold the attention of the reader. His hero identifies himself with nature. And nature reflects the emotional state of the hero. This continuous dialogue between nature and the protagonist reflects an ascending escalation of emotions: "When, finally, the young shepherd will see the object of his passion swim in the sea, the coexistence of natural elements and their impact on the feelings of the hero will convert the whole scene into a poetical, exotic place, full of poetical contradictions… Nature becomes 'magic' and the erotic and romantic tension is heightened. This scenery greatly contradicts with the oppressed present of the writer from his life in the city, something which allows Papadiamantis to exercise strong criticism on the urban transformation of Greece at the end of the 19^{th} century" [17]. In fact, Papadiamantis thinks of the city as a prison which exhausts its inhabitants and reveals his negative position on this new type of modernity [18].

Nirvanas describes a moment with Papadiamantis which shows the purity of Papadiamantis' relationship with nature and the feeling of imprisonment he had in Athens:

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I saw him – this I shall never forget – run behind the sun, as a youngster in love runs behind his mistress. This was one of the most tragic things I had seen in my life. And, I may say, not even a work of art could move me as tragically as the sight of Papadiamantis running behind the sun… It was an autumn sunset and the sun was setting in melancholy behind Acropolis. I then saw Papadiamantis walk fast towards the columns of the Temple of Olympian Zeus. Papadiamantis without stopping at all told me bitterly…

-Leave me alone! I must catch the sun before it sets. I have not seen the sun for a month. And I never catch it.

And he was running behind the sun, which was already hiding behind the mountains of Salamina. Locked until sunset in the offices of his newspaper, after leaving his office, he could no longer find the sun in Athens. And he was running to catch the sun in the open horizon, to see the sun face to face behind Acropolis, to greet him on the top of a far away mountain. And he was running behind the sun, without catching it [7].

3. SOME ACTIVE LEARNING ACTIVITIES

Students can use Papadiamantis' writings in a variety of activities. Some suggestions:

- Compare and contrast environmental issues at the end of the 19th century with environmental issues today.
- Choose one of Papadiamantis' ecologically oriented short stories. Choose an extract from the story that seems to you particularly significant. Explain the reason for your choice.
- Choose one of Papadiamantis' ecologically oriented short stories. If you had to change something in the story what would you change? Why?
- Choose an ecologically oriented short story by Papadiamantis and identify its primary message / messages? What is / are its secondary message (-es)? Justify your answers.
- Choose one of Papadiamantis' ecologically oriented short stories. What light is thrown on the story by its title?
- Choose any ecologically oriented short story by Papadiamantis. What questions does it raise?
- Choose any ecologically oriented short story by Papadiamantis. What emotions does it create? Justify your answer.
- Choose an ecologically oriented short story by Papadiamantis. As a tool for raising environmental awareness rate the story from 1 (very low) to 5 (excellent). Justify your answer.

References

[1] Koukoulommatis, D.I., 1996. *Literature and Language in Primary and Secondary Education.* Ellin, Athens.

[2] Greimas, A., 1985. Transmission and communication. *Serizi Conference, The Teaching of Literature.* Epikairotita, Athens, 27-40.

[3] Marsh, E.J., Meade, M.L., Roediger, H.L.I., 2003. Learning facts from fiction. *Journal of Memory and Language,* **49,** 519-536.

[4] Prentice, D.A., Gerrig, R.J., 1999. Exploring the boundary between fiction and reality. *Dual-process Theories in Social Psychology* (eds S. Chaiken and Y. Trope), Guilford Press, New York, 529-546.

[5] Green, M.C., Brock, T.C., 2000. The role of transportation in the persuasiveness of public narratives. *Journal of Personality and Social Psychology,* **79 (5),** 701-721.

[6] Naki, S., 2012. Environmental education and literature: The role of literature in building positive attitudes towards the environment. A didactic trial in the course Modern Greek Literature in the 1st grade of high school.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros, C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas

ISBN: 978-960-6865-94-7

Proceedings of the Greek Institute of Applied Pedagogy and Education, 6th National Conference, October 5-7, Athens. http://www.elliepek.gr/documents/ 6o_synedrio_eisigiseis/34_Naki.pdf
[7] Kantaraki, S.D., 2016. Papadiamantis as a stimulus for environmental awareness and environmental education. http://www.24grammata.com/wp-content/uploads/2012/07/Kantaraki-Papadiamòanth-oikologia-24grammata.com_.pdf (accessed March 11, 2016)
[8] Collie, J., Slater, S., 1991. *Literature in the Language Classroom.* 5th ed. Cambridge University Press, Glasgow.
[9] Kanatsouli, M., 2005. Ecology and children's literature. *Environmental Education: The Coming New Civilization…* (ed A. Georgopoulos), Gutenberg, Athens, 535-549.
[10] Lekati, E., Baltatzis, E., Baltatzis, D., 2014. Alexandros Papadiamantis, an all-time great educator. *Proceedings of the Greek Institute of Applied Pedagogy and Education*, 7th National Conference, 10-12 October. http://wwwelliepek.gr/documents/7o_synedrio_eisigiseis/ lekath%20mpaltatzhs-h.pdf (accessed March 11, 2016)
[11] Egglezos, C., 2011. Alexandros Papadiamantis – 2011: Year of Papadiamantis. 27 May. http://www.sed.gr/forum/viewtopic.php?t=3392 (accessed March 24, 2016)
[12] Kantaraki, S.D., 2011. The nature loving element in Papadiamantis' short stories in education. *4th International Conference on Papadiamantis.* 1 October. http://www.24grammata.com/ ?p=19438 (accessed March 2, 2016)
[13] Nikitara, C., 2016. The didactic exploitation of the environment in the literature readings in secondary education. http://users.sch.gr/xnikhtara/nikitar_txt01.html (accessed March 16, 2016)
[14] Keselopoulos, A., 1991. The natural environment in Papadiamantis. *Anti*, 46-51. http://digital. lib.auth.gr/record/16106/files/npa-2005-15668.pdf (accessed March 22, 2016)
[15] Pantazis, V.E., 2004. Introduction to an anthropological-pedagogical understanding of nature in the work of Papadiamantis. *Proceedings of the 1st National Environmental Conference,* 7-9 May 2004, Orestiada, 797-804.
[16] Literature for the theoretical direction, 2016. http://reviews. in.gr/files/1/2011/ rootfiles/log_140311.pdf (accessed March 16, 2016)
[17] Baxevani, E., 2012. Nature and man in the short stories of Papadiamantis and Viziinos. 29 April. http://wwwideastudies.blogspot.gr/2012/04/blog-post_2993.html (accessed March 16, 2016)
[18] Lefaki, M., Telioni, E., 2016. The identity of the city of Athens in the urban fiction in the period 1890-1910. http://www.eens.org/EENS_congresses /2010/Lefaki_Mary&Teleioni_Eleftheria. pdf (accessed March 17, 2016)

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Leisure time and mass media among elementary school pupils: Some research findings

G. Tsantopoulos, E. Manolas*, A. Dalamagkidou

Department of Forestry and Management of the Environment and Natural Resources,
School of Agricultural and Forestry Sciences, Democritus University of Thrace,
193 Pantazidou Street, 68200 Orestiada, Greece.
*Corresponding author: Email: emanolas@fmenr.duth.gr

Abstract

The aim of this paper is to record the attitudes and views of elementary school pupils in the Prefecture of Evros as far as making best use of their leisure time is concerned, in particular through the use of the mass media. This was done through the use of a structured questionnaire which was completed by 413 pupils in the 5th and 6th year of their studies in the period May – October 2014. The results show that with regard to how to make best use of their leisure time half of the pupils decide in consultation with their parents. With regard to the activities pupils prefer in their leisure time these mainly are playing with friends or siblings and the participation in athletic associations. Watching television and using the internet is not among their main preferences because these are solitary activities and, therefore, of less interest to pupils.

Keywords: environmental communication; television; elementary school pupils.

1. INTRODUCTION

Modern man, in his everyday activities and choices, is often influenced by the mass media. This can be easily discovered through observing the daily activities of both adults and children. With regard to whether there is a relationship between information transmitted by the mass media and acquiring new knowledge, the results seem positive on the condition that rational use is made. Many support the view that the aim of the mass media, in addition to transmitting information, is to shape the views and attitudes of the respondents [1] while at the same time claiming that such impact is significant to the degree that it can both shape and modify behaviors [2].

In the era of sophisticated technology and direct and fast mass communication, it is necessary to recognize and understand the attributes of communication and of the means which make this communication possible. This is necessary in order to understand the continuously increasing use of these mass media and of the information they transmit. With regard to the environment, information by itself cannot change views, attitudes and behaviors. This view is supported by Chapman & Sharma [3], Pruneau et al. [4] and Tsaliki [5] who think that the linking of information-theory with practice is necessary. In order to achieve the creation of positive attitudes and responsible behavior with regard to the environment, these researchers propose the use of active learning methods such as experiential, cooperative, reflective learning methods.

In the past, the family was responsible for the upbringing and socialization of the child transmitting in turn the responsibility of the education of children to schools. After the above institutions, the forces completing the education of man were experiential learning and professional life. From a different perspective modern education seems to be defined from the interdependence, interrelationship and contribution of at least three important factors [6]: a) family, b) education, c) the so called parallel school which refers to social life as a whole, but also to the totality of the mass media of communication with emphasis on the press, radio, television and currently the internet.

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The original position, regarding the impact of the mass media on the population, is strengthened, among others, by the research of Keefer & Khemani [7], with positive results on the issue of the literacy of pupils due to access to the mass media. In particular, this research was carried out in Benin of Africa, where frequent access to many local radio stations was linked to the rapid increase of literate pupils in villages of the area, but also to the increasing interest of families for educating their children. According to them, information and persuasion from access to the mass media can be achieved "either directly, via exhibition of individuals to them, or indirectly, via social networks or other social institutions" [7]. Also, the results of the research of Kirilenko et al. [8] regarding the influence of mass media and local temperature on the discussion concerning climate change on Twitter – means of social networking – are similar: "weather and the news produced by the mass media control public interest on climate change". However, the above research cannot prove that the mass media constitute the intermediary-instigator of discussion with regard to this particular means of social networking. With regard to acquiring new environmental knowledge, according to Aini & Fakhru'l-Razi [9] who researched Malaysian secondary school students who participated in the National Environmental Education Curriculum during their elementary and secondary education, the main source appears to be television. According to Vryzas [10] television originally played a dominant role in relation to children who were passive receivers of the transmitted messages. Soon, however, this view was questioned and research focused on the child and the way the child uses television with regard to his needs, expectations, potential and particularities, supporting that the impact of television is neither decisive nor of minor importance. With regard to parental control of television viewing, the pupils of upper social classes are under stricter control in relation to pupils of middle and lower classes. This is most likely due to inadequate information or fatigue from work of the parents of pupils of middle and lower social classes.

With regard to the role of mass media for education-learning, this has also been recognized by the UN inter-governmental conferences which classify them as non-formal and informal education. In particular, as the problems were becoming bigger and as new needs were appearing and societies were constantly evolving, these international conferences were materialized in the framework of formulating international environmental policy. During the same decade – 1970s – after the fall of the junta in Greece, citizen mobilization and interest on the environment and its protection begins to become a reality.

The aim of this paper is, on the one hand, to present the views of elementary school pupils with regard to their daily habits and interests and, on the other hand, to identify the factors which will contribute to more effective management of their leisure time.

2. MATERIALS AND METHODS

For the collection of data regarding the views and attitudes of pupils of the 5th and 6th grade of elementary schools in the prefecture of Evros a questionnaire with closed questions was used. This research constitutes part of a larger research project in which the questions are classified in five categories, which are: 1) activities-interests of pupils and the role of parents, 2) means of information-communication, 3) knowledge of pupils on environmental matters, 4) habits of pupils and their families and 5) demographic characteristics of the child and the parent. Regarding the interests of the pupils the categories examined were: QB_1=Pleasure/ Entertainment, QB_2=Personal matters (Your family, your friends, etc), QB_3=Athletics, QB_4= Education (Courses inside and outside school), QB_5=For nature, QB_6=Social matters (Regarding human relations around you – among them and with you), QB_7=Economic matters. Regarding the best possible use of the pupils' leisure time the categories examined were: QA_1=Do you play with your friends/siblings? QA_2=Do you participate in athletic/cultural/social associations or academies? QA_3=Do you surf in the internet? QA_4= Do you play electronic games? QA_5=Do you listen

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to/play music? QA_6=Do you watch television? QA_7=Do you read books/magazines? QA_8=Do you play table games? QA_9=Do you draw? QA_10=Do you play games by yourself? QA_11=Do you make handicrafts? The sample was seventeen (17) elementary schools of the Prefecture of Evros while 412 questionnaires were completed by 5th and 6th grade pupils. Regarding permission to conduct the research the researchers followed the guidelines provided by the Pedagogical Institute [11]. The collection of data was done during the period May-October 2014. For purposes of data processing descriptive statistics, Friedman's non-parametric test and categorical regression were used. Also, the researchers used the statistical programme SPSS.

In the research, Cronbach's α coefficient is used to identify the internal consistency of a questionnaire, i.e. whether the data have the tendency to measure the same fact. It expresses the squared correlation between the score (observed) that a person is assigned on the given scale and the score that they would have obtained (true) if they had been asked about all issues [12]. The Friedman test is used to compare the values of three or more correlated groups of variables. The distribution of the Friedman test is a X^2 distribution with (df) df = k-1degrees of freedom, where k is the number of groups or samples. This test classifies the values of variables for every subject separately and calculates the mean rank of classification values for each variable [13,14]. The Friedman test was used for the multidisciplinary variables "best possible use of leisure time" (QA) and for the "interests of pupils" (QB). Categorical regression is an extension of the principles of classical linear regression and logarithmic analysis. Through scaling, it assigns values to each category of variables in such a way that they are optimum as concerns the regression, and reflect the characteristics of the original variables. Categorical regression scales the nominal, ordinal and numerical variables in an optimum manner, quantifying their categories, so that the squared correlation between the quantified dependent variable and the linear combination of the quantified independent variables is maximized. The interpretations are related to the transformed variables, but they are also related to the original variables, due to the relation that exists between the original variables and the transformed ones [15]. Categorical regression was applied three times with the dependent variables being a) the participation of parents in the activities of their children, b) the extent to which children watch television together with their parents, c) whether parents supervise the use of internet. The independent variables were the sex of the person asked, the level of education and the profession of the parents of the children.

3. RESULTS

The primary data collected and presented in this research concern the attitudes and views of pupils for a series of matters such as pleasure and best possible use of their leisure time, who decides for their leisure time, the participation of parents in the activities of their children, the extent to which they watch television together with their parents, if there is parental control during the use of the internet, their interests, and the ways they make best possible use of their leisure time.

The classification of the interests of pupils resulted after the application of the Friedman test. After the application (N=412 Chi-Square=429.818 df = 6 Asymp. Sig = 0.000) (Figure 1) and with the co-efficient a-Cronbach being 0.771, we see that the main subject of the multidisciplinary variable "interests of pupils" is "Entertainment / Pleasure" with a mean rank of 4.86. Second in the classification of interests is "personal matters", then "athletic matters" while fourth is "educational matters related and unrelated to school".

With regard to making the best possible use of their time 69.6% declare "much" to "very much" pleased from the way they make the best possible use of their leisure time while 26.7% of them seem to be "fairly" satisfied from their choices. Only 3.7% of the pupils declare that they are "little" to "not at all" satisfied from the way they make the best possible use of their leisure time (Table 1).

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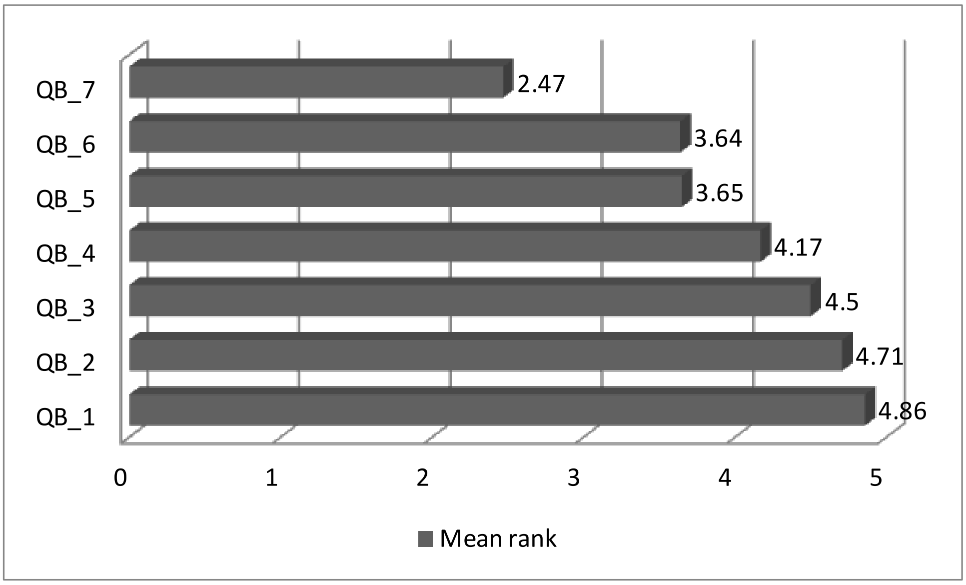


Figure 1. Application of Friedman test regarding the interests of pupils.

Table 1. Percentage analogies regarding pleasure from best possible use of leisure time.

Percentage (%)	
Not at all	1.0
Little	2.7
Fairly	26.7
Much	27.9
Very much	41.7
Total	100.0

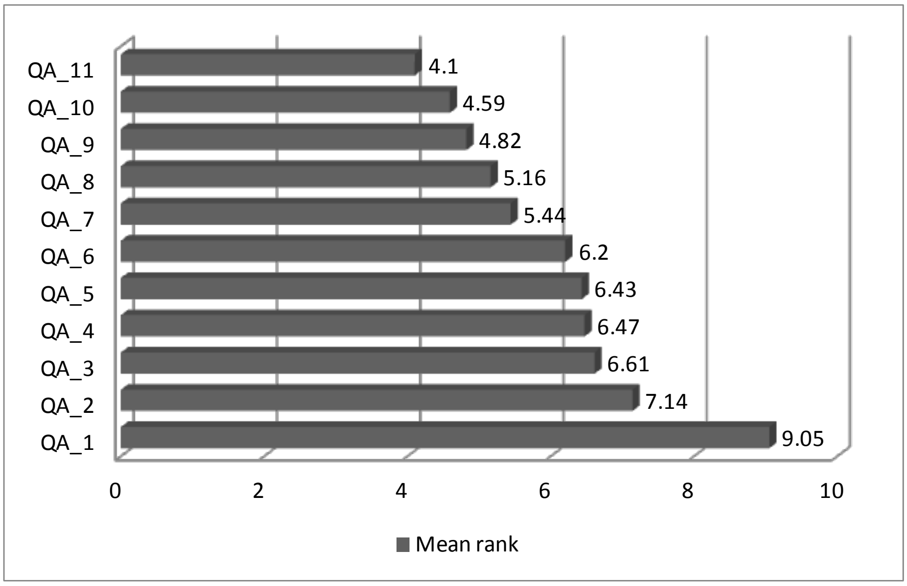


Figure 2. Application of Friedman's test regarding the best possible use of leisure time.

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The next subject investigated was the preferences of pupils regarding activities in their leisure time. In order to make possible the classification among preferences and to find out if there is statistical difference among differences, the Friedman test was applied. However, before the application of Friedman's test the co-efficient a-Cronbach was extracted which was 0.678. According to the results of the above test (Friedman test: N= 412 Chi-Square= 809.65 df = 10Asymp. Sig = 0.000) (Figure 2), it was found that "games with friends or siblings" is the first choice of preferred activity regarding making the best possible use of the leisure time of pupils, with a mean rank of 9.05. The second choice is "participation in various associations", while in the third and fourth choice we have "surfing in the internet" and "watching television".

Table 2. Percentage analogies regarding choice of leisure time activities.

Percentage (%)	
Your parents	1.9
By yourself	50.5
Your parents and you together	47.6
Total	100.0

According to table 2, which refers to the person /persons who chooses/choose the activities of the pupil, it was observed that 50.5% of the pupils decide "by themselves" for their activities while 47.6% declares that they decide jointly with their parents on the best possible use of their time. For a very small percentage, i.e. 1.9%, it is the children's parents who decide for their activities. Only 3.9% of pupils declare that their parents "always" participate in their activities, 65.0% think that their parents participate "sometimes" and almost one to three pupils (31.1%) declare that their parents "never" participate in their activities (Table 3).

Table 3. Percentage analogies regarding participation of parents in the activities of pupils.

Percentage (%)	
Always	3.9
Sometimes	65.0
Never	31.1
Total	100.0

Table 4. Percentage analogies regarding joint viewing of parents-pupils.

Percentage (%)	
Always	17.2
Sometimes	80.1
Never	2.7
Total	100.0

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Table 5. Percentage analogies regarding supervision of pupils during their use of the internet.

Percentage (%)	
Always	7.0
Sometimes	49.3
Never	43.7
Total	100.0

The viewing of television programs jointly with parents is done only by 17.2% of the pupils while 80.1% think that this is happening "sometimes" (Table 4). Only 7.0% of the pupils declare that they "always" surf in the internet in the presence of their parents, 49.3% think that this is happening "sometimes" and, finally, 43.7% of the pupils declare that the parents "never" supervise them during their use of the internet (Table 5).

Subsequently, categorical regression was applied in order to investigate whether the pupil's sex, the pupil's grade, the father's and mother's profession as well as the educational level of the father and mother impact the participation of parents in leisure time activities, joint viewing of television by parents and pupils and parental control of surfing in the internet.

Table 6. Categorical regression results in relation to whether or not parents participate in the activities of the pupil during their leisure time.

	Standardized Coefficients		**F**	**Sig.**	**Importance**
	Beta	**Bootstrap (1000) Estimate of Std. Error**			
Sex of pupil	-0.030	0.049	0.376	0.540	0.009
Grade	**0.101**	0.049	4.224	**0.041**	**0.135**
Father's profession	**0.089**	0.049	3.296	**0.006**	0.095
Mother's profession	**-0.096**	0.052	3.462	**0.002**	0.095
Father's educational level	**-0.279**	0.061	**20.895**	**0.000**	**0.652**
Mother's educational level	0.149	0.063	5.619	**0.000**	0.014

Table 6 presents the results of categorical regression with the dependent variable being the participation of parents in children's leisure time activities. The independent variables are the individual characteristics of the pupil and his parents. The standardized regression coefficients of the independent variables show that the participation of parents in the activities of their children is influenced more by the variables mother's profession, father's profession and mother's educational level and grade. The removal of variables which present a high value F weakens the model while the impact of removal of the variable sex on the predictability of the model is negligible. In addition, the measures of relative importance of the independent variables show that the variables father's profession (65.2%) and grade (13.5%) have greater impact on the dependent variable. During the transition from lower to higher educational levels of fathers we see greater participation in the activities of the children while the opposite happens with the educational level of mothers, i.e. the higher the educational level of mothers the smaller the participation in leisure time activities.

In the case of the dependent variable, of parents and children jointly watching television (Table 7), from the standardized regression coefficients we see that this is affected more by the variables mother's and father's profession and mother's educational level. The measures of relative importance of the independent variables show that the variables father's profession (36.9%), mother's profession (32.1%) and educational level of mother (31.0%) have greater impact on the dependent variable. The signs of the standardized regression coefficients and the transformation

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diagrams of each variable, for the professions of both fathers and mothers, show that the more a profession is characterized by fixed working hours, e.g. profession of servants and mainly public servants, the more these people watch television together with their children. On the other hand, we see that as we go up the mothers' educational levels the amount of joint television viewing is decreasing.

Table 7. Categorical regression results in relation to parents and children watching television together.

	Standardized Coefficients		F	Sig.	Importance
	Beta	**Bootstrap (1000) Estimate of Std. Error**			
Sex of pupil	0.088	0.049	3.231	0.073	0.128
Grade	-0.028	0.049	0.332	0.565	0.019
Father's profession	**0.149**	0.049	**9.170**	**0.000**	**0.369**
Mother's profession	**0.143**	0.050	**8.265**	**0.000**	**0.321**
Father's educational level	-0.063	0.055	1.281	0.258	0.000
Mother's educational level	**0.102**	0.056	**3.370**	**0.019**	**0.163**

Table 8. Categorical regression results in relation to whether or not the child when surfing in the internet is under the supervision of parents.

	Standardized Coefficients		F	Sig.	Importance
	Beta	**Bootstrap (1000) Estimate of Std. Error**			
Sex of pupil	-0.042	0.049	0.720	0.397	0.011
Grade	0.067	0.049	1.886	0.170	0.062
Father's profession	**0.141**	0.050	8.074	**0.000**	**0.240**
Mother's profession	**-0.106**	0.051	4.417	**0.000**	**0.125**
Father's educational level	**-0.229**	0.066	12.209	**0.000**	**0.250**
Mother's educational level	**0.251**	0.065	14.715	**0.000**	**0.310**

Finally, with regard to the dependent variable of parental control concerning surfing in the internet (Table 8), from the standardized regression coefficients of the independent variables it is found that parental control regarding surfing in the internet is not affected by the variables, sex of pupils and grade. The measures of relative importance of the independent variables show that the variables mother's educational level (31.0%), father's educational level (25.0%), father's profession (24.0%) and mother's profession have greater impact on the dependent variable. The signs of the standardized regression coefficients and the transformation diagrams of each variable for the professions of fathers show the more a profession has fixed working hours the more the fathers engage in joint television viewing with their children. The opposite happens with regard to mothers. Finally, there is a contradiction on the issue of parental control with regard to surfing in the internet which is due to the educational level of the father and the mother. In particular and with regard to fathers as we go up the educational levels the more the parental control regarding surfing in the internet while the opposite happens with regard to mothers.

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4. CONCLUSIONS AND DISCUSSION

The aim of this paper was to investigate the issues which directly or indirectly affect how pupils of elementary schools make the best possible use of their time. This was achieved: the analysis which was carried out identified all the factors which can possibly improve the existing situation and constitute a valuable tool for the educational community.

The majority of the pupils are satisfied from the way they make best use of their leisure time while the parents play an important role in the shaping and management of leisure time. The parents themselves participate, supervise the use of television and internet and advise their children on the type of activities they should choose. With regard to the type of activities pupils prefer in their leisure time, playing with their friends or their siblings is the most important activity, which is something which strengthens the social nature of man and his tendency to seek companionship for purposes of communication and entertainment [16]. An activity which also seems to be important is participation in academies or athletic/cultural/social associations which can also be explained on the grounds the previous one was. The viewing of television and the use of the internet are not among the first preferences since they are individual and less interesting activities for pupils. As Koumentos [17] points out children with out of school interests spend fewer hours watching television in relation to children who do not engage themselves with other activities. At the same time, the main interests of pupils of this age are found to be entertainment, pleasure and various personal matters relating to their family and friends. The natural environment is not among the main interests of pupils despite the education they receive from the school on this issue.

Finally, with regard to making the best possible use of leisure time but also the daily habits of pupils, these are examined separately from parents. They are also influenced more by the profession of the parents and less by the educational level of parents while they are not at all affected by the sex and age of the pupil. The results from the non-rational use of leisure time do impact the personality of the child originally in the school and then in society. Thus, teachers are the first to find out but also experience the consequences of the above problem and also deal with these consequences. Therefore, the use of the results of this research paper may prevent or rectify undesirable situations which in different circumstances may have irreversible effects.

References

[1] Skanavis, C., 2004. *Environment and Communication: Having the Right to Choose*. Kaleidoskopio, Athens.

[2] Marantos, P., 1999. *Education and Media of Mass Communication: The Use of the Mass Media in Education.* PhD Dissertation. Department of Sociology, Panteion University of Social and Political Sciences, Athens.

[3] Chapman D., Sharma K., 2001. Environmental attitudes and behavior of primary and secondary students in Asian cities: An overview strategy for implementing an eco-schools programme. *The Environmentalist*, **21**, 265–272.

[4] Pruneau D., Doyon A., Langis J., Martin L., Ouellet E., Boudreau G., 2006. The process of change experimented by teachers and students when voluntarily trying environmental behaviors. *Applied Environmental Education and Communication*, **5**, 33–40.

[5] Tsaliki V., 2005. "…For the sake of the environment…" Words or deeds? *Environmental Education: The coming new civilization* (eds A. Georgopoulos), Gutenemberg, Athens, 279-292

[6] Mialaret, G., 2002. *Introduction to Education Sciences*. Tipothito – Giorgos Dardanos, Athens.

[7] Keefer, P., Khemani, S., 2014. Mass media and public education: The effects of access to community radio in Benin. *Journal of Development Economics*, **109**, 57 – 72 .

[8] Kirilenko, A., Molodtsova, T., Stepchenkova, S., 2015. People as sensors: Mass media and local temperature influence climate change discussion on Twitter. *Global Environmental Change*, **30**, 92 – 100.

[9] Aini, M. S., Fakhru'l-Razi, A., 2007. Environmental comprehension and participation of Malaysian secondary school students. *Environmental Education Research*, **13 (1)**, pp. 17–31.

[10] Vryzas, K., 1997. *Means of Communication and Childhood.* Vanias, Thessaloniki.

[11] http://www.pi-schools.gr/structure/departments/tetet/kritiria. php (accessed February 10, 2014).

[12] Siardos, G., 1999. *Multivariate Statistical Analysis Methods*. *Part I: Exploring the Relations among Variables.* Zitis Publications, Thessaloniki.

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[13] Freund, R., Wilson, W., 2003. *Statistical Methods*. Elsevier, New York.
[14] Ho, R., 2006. *Handbook of Univariate and Multivariate Data Analysis and Interpretation with SPSS*. Chapman & Hall, USA.
[15] Siardos, G., 2000. *Multivariable Statistical Analysis Methods*. *Part II: Exploring the Dependence among Variables.* Siardos, Thessaloniki.
[16] Bakirtzis, K. 2006. *Communication and Education.* Gutenberg, Athens.
[17] Koumentos, G., 2006. The impact of television on leisure time and academic performance of elementary school pupils: An empirical research. *Epistimoniko Vima*, **6**, 136 – 151.

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How close to being “Green” are the Greek universities

D. Papaioannidou, C. Sardi*, A. Kounani, C. Skanavis

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
* Corresponding author: Email: env12078@env.aegean.gr

Abstract

In the last two decades the concept of sustainable development (SD) has been attracting intense interest around the globe with the focus the adoption of a daily routine and connecting environmental decisions to social, political and economic factors. Universities should probably be front-runners into analyzing the importance of an SD policy, due to the fact that they cultivate the future leaders and decision- makers. There is a lack of clarity on how each institution defines SD and how the related policy is incorporated into their daily routine. On the basis of the conventional terminology, the “Green” only specifies the environment, while SD indicates environmental, economic and socio-cultural aspects. In terms of putting it into practical action there is a major difference between being Green and having an SD policy in effect. This research focuses on the Greek Academic Institutions in order to find out how close to being actively Green the universities are.

Keywords: green universities; sustainable development policy; Greek universities; Greece

1. INTRODUCTION

1.1 Definition of SD

Nowadays the world is confronting a civilization crisis, which is leading to an intimidating future. One of the biggest national and global challenges that people will have to deal with in the near future is that they will have to espouse a more sustainable way of life [1].

Definition of SD: The general features of SD associate environmental perceptions with social and economic growth [2,3,4,5,6]. The most distinguished definition of the term SD is written by Brundtl in his report with the title ‘Our common future’: ‘Sustainable development is development that meets the needs of the present, without compromising the ability of future generations to meet their own needs’ [7]. The dynamics and manifestations of SD vary depending on the scenario that we find it in. Therefore the meaning of SD is constantly being adjusted, causing some confusion [2]. The term sustainability (SD), is used by many groups even with conflicting interests and radically different ideas [8].

According to the ‘Framework for the UNDESD International Implementation Scheme’ [3] there are three main dimensions (environmental, social and economic), in relation with education and learning for SD:

- Socio-cultural perspectives: human rights, peace and human security, gender equality, cultural diversity and intercultural understanding, health, HIV/AIDS and governance
- Environmental perspectives: natural resources (water, energy, agriculture, bio-diversity), climate change, rural development, sustainable urbanization and disaster prevention and mitigation
- Economic perspectives: poverty reduction, corporate responsibility and accountability in the market economy [3].

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Sustainable Development aims to maintain economic progress along with the protection of the long-term environmental value. The above aim can be achieved through the integration of environmental policies and development strategies [7].

1.2 SD policy at universities

The Universities as leaders of new and innovative practices provide a basis for systematic initiatives and actions by establishing Sustainable Policy [9]. According to Ciferri and Lombardi, Policy Development and strategy need to encourage a new way of thinking through the educational system [10]. The areas that could be included into the framework policy at university level according to Lozano [11] are the following: Research, Campus operations, curricula, community outreach, assessment and reporting, University collaboration, installing SD in the daily campus experience (education and educators) and generally installing SD into the institutional framework. Each of these areas is a part of a common policy framework, but some areas in order to be more effective should apply sub-policies. Institutional framework must insure that sub-policies don't lead to the fragmentation of the general process, but should work as a unified component in order to achieve the integrated view of SD.

1.3 Importance of implementing SD into university level

1.3.1 A rising importance of implementing SD into universities through the decades

The first official declaration that was made by university administrators and which established the commitment to environmental sustainability in higher education was the Talloires Declaration in France in 1990. At the Rio Summit in 1992, the urgency of promoting education, public awareness and training was highlighted: "Education is critical for promoting Sustainable Development and improving the capacity of the people to address environment and development issues" (Chapter 36 of Agenda 21). Chronologically the next declaration which influenced higher education to include sustainability in education and in general activities of the citizens was the Kyoto Declaration of 1993, which was also approved by 90 universities from all over the world [12]. This idea was furthermore supported globally by UN initiatives, with the most important the current Decade of Education for Sustainable Development (2005–2014). The aforementioned declarations have been nationally executed, through legislation [13,14], government policy [15], government funding of Higher Education initiatives [16] and through partnerships with non-governmental organizations [15,17].

Another notable declaration that should be mentioned is the biggest United Nations (UN) conference, which took place in Rio de Janeiro in June 2012 and which was followed by 46,000 delegates and a further 50 million people taking part through live streaming and social media. The outcome document of Rio+20 conference was titled 'The future we want' and acknowledges the significance of 'education at all levels', by encouraging institutions to embrace good practice by adopting a way of teaching based on sustainable development integrating components across disciplines, and by undertaking research in this area.

1.3.2 Importance of implementing SD in Universities as significant social actors

Universities as critical social multipliers must develop their role much stronger as models for society in the pursuance of sustainability. Furthermore, by the conservative use of resources, universities offer a professional initiative that saves money and safeguards reputation [18]. Universities are key places for progressive action to address this global issue within current and future generations by graduating world leaders in research, innovation, and education [19]. The core factors that make universities remarkably responsible for SD are their academic freedom and the effect they have on society [20].

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1.4 Difference (misunderstanding) between university with SD policy and greening the campus

Many Universities call themselves “Green”, but it takes more to have a University with a real SD Policy.

1.4.1 How does a “sustainable university” look like?

In general terms, a university consciously choosing the path of sustainable development would exemplify the following principles:

- Clear articulation and integration of social, ethical and environmental responsibility in the institution’s vision, mission and governance;
- Integration of social, economic and environmental sustainability across the curriculum, commitment to critical systems thinking and interdisciplinary approach, sustainability literacy expressed as a universal graduate attribute;
- Dedicated research on sustainability topics and consideration of “quadruple bottom line” sustainability aspects in all other research;
- Outreach and service to the wider community, including partnerships with schools, government, non-governmental organizations and industry;
- Campus planning, design and development structured and managed to achieve and surpass zero net carbon/water/waste, to become a regenerative organization within the context of the local bioregion;
- Physical operations and maintenance focused on supporting and enabling “beyond zero” environmental goals, including effective monitoring, reporting and continual improvement;
- Policies and practices which foster equity, diversity and quality of life for students, staff, and the broader community within which the university is based
- The campus as a “living laboratory” – student involvement in environmental learning to transform the learning environment;
- Celebration of cultural diversity and application of cultural inclusivity; and frameworks to support cooperation among universities both nationally and globally.

There is a lot of ambiguity in the concept and the agenda of ‘green’ university. For example, having built one showcase green building is by far different from having a university committed to build only green buildings across campus-the first is a project success, the latter a systemic conversion [20], which is more advisable for sustainability. Universities are in a position to embrace sustainable/green university strategies, which would eventually establish sustainability principles [21].

“Campus greening” has become mainstream, and this is something to be concerned about [22]. Therefore, it is now common to see in most universities worldwide, innovative examples of environmental actions such as: green building design, recycling and reusing, energy efficient lighting, water conserving fittings and public conveyance initiatives.

1.4.2 How sustainable university projects are different from greening the campus programs

Greening the campus programs requires a multi-stakeholder approach, while SD projects rely on trans-disciplinary research partnerships. “Green University” does not only focus upon the ecological aspects of sustainability but also on other aspects such as research and development, education, staff rewards, etc. Although there is growing attention and action on sustainable development in higher education, there is no clear definition of “Green University”.

Many institutions establish campus greening initiatives, such as environmental education programs/courses and conducted environmental research in addition to their existing academic activities in response to calls for higher education to lead society towards sustainable development. The factors that structure a “Green University” can be broadly grouped into seven categories, i.e. management systems, environmental sustainability, sustainable curricula, research and develop-

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ment, staff development and rewards, student opportunities and social responsibility. Higher Education Institutions (HEI) struggle to provide a holistic approach to cover the full range of operating one university and show the superiority of action mix over single measures. While valuable, this could only be considered a first step [1,23,24]. Besides physical projects, such as wastewater recycling and source separation for solid wastes, green education and research activities should also be incorporated into the overall action plan so that all the stakeholders can improve their awareness and actively participate in various efforts.

1.5 Factors influencing the implementation of SD

According to Amaral, Martinsand Gouveia [25], "despite the fact that operational initiatives can be seen as worthy examples of sustainable practices, they cannot by themselves be a guarantee of campus sustainability. They lack a systematic and continuous quality improvement approach that is the core of the standardized management systems". However, changing attitudes and behavior is a difficult and complex task. Recent research findings suggest that it takes more than just information dissemination to influence and change attitudes [9].

Incorporating sustainability into a university system presents challenges regarding its education, research, operations and outreach dimensions [26]. These challenges and opportunities are factors that influence the activation of an SD policy. The ones that are investing into Education SD have recognized that their role is not only to educate future societal leaders, decision-makers, and intellectuals, but that they themselves should be learning organizations practicing sustainability in education, research, outreach and campus facilities management [1]. Lack of information on environmental problems may be a major obstacle during environmental policy applications, which in turn deprives the university community from experiencing the benefits deriving from environmental management initiatives [27].

Resistance to change is another factor that influences application of an SD policy at a university. Academic freedom, the tradition of criticism and tenure, common cultural characteristics at universities, maneuver change and resistance to SD. It is not unusual to have senior academics whose academic futures are assured, accustomed to influence and prestige not to embrace or want change. However, a good number of junior academics strive to achieve acceptance, innovation and new ways of working. Change in universities is strongly connected to organizational politics. Recognition of related barriers helps identifying the types of action needed to ensure successful change efforts and implementation of sustainable development policy [28].

2. METHODOLOGY

2.1 Research area

In order to gain a comprehensive view of the prevailing situation in HEI's in Greece, we conducted a survey in which we attempted to investigate how close to being "Green" the Greek universities are.

2.2 Research instruments

This research was based on a series of questions, which in the first instance was investigated through the sites of each university as the first step of our research and the second level was the confirmation of the data collected by the rector authorities.

Once we collected the data, we proceeded to classify it according to the type of questions and then we correlated the results by using the SPSS program.

2.3 Research sample

The research was conducted nationwide. More specifically, it concluded all Higher Academic Institutions of Greece, which are 23 in total.

3. RESULTS

The results revealed that 26% of Greek universities have institutionalized SD Policy. And 65% of the participants stated that their university has procedures for campus greening (e.g. energy saving programs, waste prevention and/or management schemes, environmentally friendly dormitories, etc.). In the question related to whether the sampled university has procedures for the integration of sustainable development (SD) issues in the curriculum, the results showed that 83% do. When asked if they have a systematically established SD network to link up staff, 48% of them gave positive answers. Also on the question assessing if they have procedures for training of staff on matters related to SD (e.g. formal series of seminars, guest lectures, courses, etc.), 65% answered yes. Thirteen percent of the participating universities stated that they have official procedures for SD considerations in purchases, contracting, catering and other services. The percentage of universities having official procedures for students' engagement on matters related to SD is 52%. A total of 61% of the participating universities responded that they have official procedures for joint SD activities with local actors (e.g. NGOs, municipality, regional government, etc.). Finally, 39% of universities have official procedures for international SD networking.

4. CONCLUSIONS

Out of the 23 universities in Greece, there was a response from 17 of them. Lack of information on environmental problems may be a major obstacle during environmental policy applications, which in turn deprives the university community from experiencing the benefits deriving from environmental management initiatives [27].

The assessment of data revealed that as regards to environmental policy, there is no correlation with the green campus procedures (Pearson Correlation 0,378). This result confirms that although no SD policy applies to the majority of institutions, they are recoded as green campuses based on procedures that give them the green labeling.

The investigation revealed that only 30% of Higher Education Institutions have institutionalized SD policy approved by their Senate. In contrast, the majority of universities (drawing from those not having SD policy) have established some kind of green procedures (Pearson Correlation 0,378). Analysis of the type of green procedures shows that SD training is seriously missing. Correlation with the student engagement is observed in the analysis of this work. The extent to which universities prepare students to be able to integrate social, environmental and economic considerations in future decision-making influences the implementation of a campus sustainable development policy [11].

Finally this research shows that SD policy is correlated with international SD networking (Pearson Correlation 0.504), demonstrating that the very small number of universities that offer SD policy present an interface with global trends such as institutions with international standards for sustainability. These global trends in turn affect even the universities that implement green campus procedures, without necessarily having institutionalized SD policy.

In sum, we came to the conclusion that the environmental intentions of the universities seem to be promising. Nevertheless, the application of a sustainable development policy is still far from realized.

References

[1] Ferrer-Balas D., Lozano R., Huisingh D., Buckland H., Ysern P., Zilahy G., 2010. Going beyond the rhetoric: system-wide changes in universities for sustainable societies. *Journal of Cleaner Production,* **18**, 607-610.

[2] Giddings B., Hopwood B., and O'Brien G., 2002. Environment, Economy and Society: Fitting Them Together into Sustainable Development, *Sustainable Development* **10 (4)**, 187–196.

[3] UNESCO. 2006. “Framework for the UNDESD International Implementation Scheme.” Paris: UNESCO.
[4] Gough S., 2002. Increasing the Value of the Environment: A ‘Real Options’ Metaphor for Learning *Environmental Education Research* **8 (1)**, 61–72.
[5] Rauch F., 2002. The Potential of Education for Sustainable Development for Reform in Schools. *Environmental Education Research*, **8 (1)**, 43–51.
[6] Summers M. and Childs A., 2007. Student Science Teachers’ Conceptions of Sustainable Development: An Empirical Study of Three Postgraduate Training Cohorts. *Research in Science & Technological Education,* **25 (3)**, 307–327.
[7] WCED, 1987. Our Common Future, A report from the United Nations World Commission on Environment and Development. Oxford: Oxford University Press.
[8] Jickling, B., and Wals A. E. J., 2008. Globalization and Environmental Education: Looking beyond Sustainable Development, *Journal of Curriculum Studies* **40 (1),** 1–21.
[9] Too L. and Bajracharya B., 2015. Sustainable campus: engaging the community in sustainability. *International Journal of Sustainability in Higher Education*, **16 (1),** 57–71.
[10] Ciferri L. and Lombardi P., 2009. The role of university education in fostering sustainable and responsible development, 2009 G8 University Summit Torino Declaration on Education and Research for Sustainable and Responsible Development (Turin Declaration), Torino, Italy, May 17th-19th.
[11] Lozano R., Lozano F.J., Mulder K., Huisingh D., Waas T., 2013. Advancing higher education for sustainable development: international insights and critical reflections. *J. Clean. Prod*., **48**, 3-9.
[12] Anderberg E., Nordén B. and Hansson B., 2009. Global learning for sustainable development in higher education: recent trends and critique. *International Journal of Sustainability in Higher Education*,**10(4)**, 368–378, URL: http://dx.doi.org/10.1108/14676370910990710
[13] Sammalisto K. and Lindhqvist, T., 2008. Integration of sustainability in higher education: A study with international perspectives. *Innovative Higher Education*, **32(4),** 221.
[14] Niu D., Jiang D. and Li F., 2010. Higher education for sustainable development in China. *International Journal of Sustainability in Higher Education*, **11(2),** 153–162.
[15] Nomura K. and Abe O., 2010. Higher education for sustainable development in Japan: Policy and progress. *International Journal of Sustainability in Higher Education*, **11(2),** 120–129.
[16] Scott W., and Gough S., 2006. Sustainable development within UK higher education: Revealing tendencies and tensions. *Journal of Geography in Higher Education,* **30(2),** 293–305.
[17] Wright TSA. 2002. Definitions and frameworks for environmental sustainability in higher education. *Higher Education Policy,* **15(2)**, 105–20.
[18] Copernicus Campus, 2010. Guidelines for Sustainable Development in the European Higher Education Area Prepared by the COPERNICUS-CAMPUS Sustainability Center at the Carl von Ossietzky University Oldenburg (Hans-Peter Winkelmann, Chairman) and the COPERNICUS-CAMPUS University Alliance for Sustainability, 41
[19] Finlay J. and Massey J., 2012. Eco-Campus: Applying the ecocity model to develop green university and college campuses. *International Journal of Sustainability in Higher Education,* **13 (2)**, 150-165.
[20] Ralph M. and Stubbs W., 2013. Integrating environmental sustainability into universities. *Higher Education* **67**, 71-90, DOI 10.1007/s10734-013-9641-9 (Springer Science and Business Media Dordrecht)
[21] Osmond P., Dave M., Prasad D., Li F., 2013. Greening Universities Toolkit Transforming Universities into Green and Sustainable Campuses: a Toolkit for Implementers, United Nations Environment Programme.
[22] Radford A., 2012. A critical assessment of university sustainable development policy: a Gloucestershire case study. *Earth & Environment,* **8**, 210-241.
[23] Sterling S., 2004. Higher education, sustainability, and the role of systemic learning. In: Corcoran, P.B., Wals, A. en (Eds.), Higher Education and the Challenge of Sustainability. Problematics, Promise and Practice. Kluwer Academic Publishers, Dordrecht/Boston/Londen, pp. 47-70.
[24] Koester R.J., Eflin J. and Vann J., 2006. Greening of the campus: a whole-systems approach. *Journal of Cleaner Production*, **14**, 769–79.
[25] Amaral L. P., Martins N. and Gouveia J. B., 2015. Quest for a sustainable university: a review. *International Journal of Sustainability in Higher Education*, **(16)2**, 155 – 172.
[26] Velazquez L, Mungula N, Plat A, Taddel J., 2006. Sustainability university: what can be the matter? Journal of Cleaner Production **14(9–11),** 810–9.
[27] Evangelinos K.I., Jones N. and Panoriou E.M., 2009. Challenges and opportunities for sustainability in regional universities: a case study in Mytilene. Greece. *Journal of Cleaner Production,* **17(12),** 1154-1161
[28] De la Harpe B. and Thomas I., 2009. Curriculum change in universities: Conditions that facilitate education for sustainable development. *Journal of Education for Sustainable Development*, **3**, 75-85. doi:10.1177/097340820900300115

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Environmental summer camp in a Greek Island

S. Apostolopoulou, G. Griroropoulou*, M. Karamperis, C. Skanavis, A. Kounani

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
*Corresponding author: Email: env12061@env.aegean.gr

Abstract

Nowadays, many researchers have proved that environmental summer camps could help children to become acquainted with nature and develop environmental values. This paper aims into analyzing a comprehensive thirty-day environmental summer camp- its operations and effectiveness in promoting responsible citizenship behavior. The instructional program is aimed at children between 6 to 13 years old, residing on Greek islands. This review examines an environmental summer camp on the island of Skyros, as a case study. The study incorporates participant survey data; interviews will be conducted with the attendees. The change of knowledge and environmental awareness, prior to and at completion of this summer camp, will be assessed. The goal of this project is to develop an environmental educational program that would be delivered as a summer camp and design the evaluation tools that would assess its effectiveness into shaping children's environmental behaviors.

Keywords: environmental summer camp; Skyros Island; Greece

1. INTRODUCTION

Since the 18th century the relationship between nature and man has changed its core, as humans and technological innovations have been in obvious contrast as far as what is acceptable to waste or use from energy resources. Nowadays, the natural environment is used as a deposit of wastes for the satisfaction of the ever-growing human needs. Therefore, the first signs of the modern ecological crisis can be observed [1].

As long as the environmental degradation of the planet continues to be an issue, the quality of human life is bound to deteriorate [2]. The need for radical change in the relationship between nature and man is now imperative. Furthermore as the capitalistic/consumer theory spreads over the world, we are now facing the crucial point where superficial and temporary solutions will not be enough to fix the ecological crisis to its root. According to Sterling (1996) [3] education is not just part of the solution, but it's also a big part of the problem. Also Sterling tried to bring to light the complications and problems that can be caused due to lack of the education.

If real sustainability is to become increasingly meaningful and mainstream, rather than devalued and marginalized, education in all forms and in all sectors has a vital role to play. But this requires fundamental change in education.

1.1 Forms of education and their role

Today, education is provided in three different interdependent forms: formal education, non- formal education and informal education. Formal education takes place within the formal education system (kindergarten, school, university and other schools) and leads to certified knowledge according to the educational grade the participants are at. Informal education refers to lifelong learning with which a person acquires attitudes, values, skills and knowledge through everyday experience and through the educational influence of their environment. Finally, non-formal education refers to

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every organized educational process that takes place outside of the formal system and functions as a part of a bigger process that aims to achieve certain learning goals and educational objectives [2].

1.2 Environmental education (EE)

According to the definition, given by UNESCO in 1978 at the Conference in Tbilisi, environmental education (EE) is the process of shaping a global population, which should be informed, interested in the environment and its issues, and have the knowledge, skills, attitude and will to work, as much alone as collectively, on solving the current environmental issues and preventing the appearance of new ones [4].

In order to achieve a satisfying deepening in environmental education, it is necessary to connect it to all three forms of education. Formal EE is being developed solely within the confines of the educational system (infant, primary, secondary and higher education) and is defined by the obligatory presence of the parties involved placed in learning groups according to their characteristics, such as age and level of education [2]. On the other hand, informal EE is a form of lifelong learning. During this process people come in contact with the process, clearly voluntarily, purely by their own choice. Informal EE is not confined by time or space and includes the transmission of environmental information through the media, the internet and all social contacts. Very often we use the term environmental communication [2].

Finally, non-formal environmental education, which is what we will focus on most in this paper, is the kind of intentional education that aims to developing environmental skills and attitudes, as well as, environmental ethos [5]. The main pillar of non formal EE, is the interpretation of our heritage. According to Freeman Tilden, father and creator of the interpretation of our heritage, “Heritage Interpretation” is an educational activity, which aims to reveal meanings and relationships through the actual use of the surrounding environment, by firsthand experience and by illustrative media, rather than simply to communicate factual information [6]. It is important to note that in order to complete EE successfully the aforementioned three views would have to be combined.

1.3 Responsible environmental behavior

By promoting responsible environmental behavior, we can develop the bases for the active participation of citizens of each local society in environmental issues. By the term active participation, we refer to the participation of citizens in the process of decision-making concerning such issues. It must be noted that in order to drive citizens into active decision-making participation, they need to have an informed opinion on the environmental issue of concern, something that can only be achieved which could be achieved with proper environmental education/ briefing [2].

Environmental concern and the resulting environmentally responsible behavior are affected by a complex interaction of attitudes, beliefs and socio-demographic variables. In an effort to detect, which characteristics make citizens participate in the protection and restoration of the environment, several researchers have attempted to develop models and techniques for assessing responsible environmental behavior and have shown how a behavioral manipulation of many variables can result in people’s participation in desirable environmental behaviors [7]. The greatest challenge for environmental education is to create, educate and activate motivated, conscious and committed students who behave in a consistently pro-environmental manner. The education about the environment aims not only to increase educational knowledge of the individuals but also to translate the positive attitudes about the environment into successful behavioral characteristics [7]. A knowledgeable, skilled and environmentally active citizenry is vital in resolving the environmental issues our planet is facing. Since most environmental issues are surrounded by great ubiquity, reaching a solution is difficult. Environmental literacy does not just happen, it requires a united effort by all those concerned with education to use all relevant information in order to develop and

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deliver the right programs and materials to those who are trying to influence through environmental behavior tactics [8].

1.4 Active participation

Living in a democratic country everyone has the power to decide on issues affecting the quality of his life, meaning that he has the right to influence the decisions connected to his everyday life. Regarding the decision-making processes on environmental issues public participation seems to have the greater significance of all [9].

Since 1969 the participation in environmental decision-making has been a part of the national agenda National Environment Policy Act (NEPA) in the United States. Subsequently, through international forums, such as the United Nations and the World Bank, the movement to involve citizens in environmental policy has spread to other countries as well. Simultaneously, an increasing focus on matters of public participation had been led by controversies over a wide variety of environmental issues, like natural resources management, land use, environmental justice and climate change. The goal of participation is to improve the quality, legitimacy, and capacity of environmental assessments and decisions [10].

Therefore, it is becoming perceptible that the active participation of citizens in the environmental issues of concern is the best way to deal with arising problems. Every citizen can participate on the protection of the environment, individually or in groups, through organizations either with a well-structured legislative frame or without one [2,11]. Also the participation gives the right of opposition in any decision and especially if it has been taken in the bodies of relevant administration. A governmental decision is not legalized and successfully enforced without the support of citizens. However, when citizens do not react in the decisions that do not agree with, it is recorded as a silent approval of the decision in question [2].

1.5 Outdoor environmental education

Increasing environmental knowledge level, promoting favorable environmental attitude, enforcing environmental awareness, changing environmental behavior, supporting active participation in the solution of environmental problems etc., are varied outputs, named as 'elements of environmental literacy', that bring about different approaches in environmental education [12,13,14,15,16,17].
Outdoor Environmental Education (OEE) is one of the ways of succeeding environmental literacy [12,18]. Within OEE, the natural environment is used as real conditions hands on laboratory. It has been found that nature-based outdoor education programs are effectively improving environmental awareness and sensitivity towards the natural environment. The OEE is supported by the Environmental Education and Training Partnership and is not just a fun type of program, but it is based on solid educational structure and concrete theory [12].

Recently outdoor education has become an important teaching method in order to increase environmental awareness. OEE focuses on first hand experiences outside the classroom walls, with the aim of achieving better understanding of complex environmental relationships and sustainable development. Having knowledge and being aware of environmental problems are important skills in order to understand the complex environmental relationship [19].

1.6 Environmental education in Greece

In Greece formal environmental education in the mandatory grades of education (primary and secondary) hasn’t fully reached the desired results on a responsible environmental behavior of participating students.

In summer of 2015, an environmental campaign program was designed and delivered at the island of Skyros, from the Research Center of Environmental Communication and Education, of the Department of Environment at the University of the Aegean. During its first year operation, an environmental camp for children was also offered to the local community children. The project was

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known as SKYROS 2015 and it is going to be repeated this summer as well as SKYROS 2016 project.

The purpose of this paper is to analyze the operation set up and the effectiveness in promoting responsible citizenship behavior, of a thirty day environmental summer camp on the island of Skyros under the project SKYROS 2016. In addition to this, it is going to assess the change of knowledge and environmental awareness, prior to and at completion of this summer camp. The main goal of this project is to develop an environmental educational program that could be delivered as a summer camp. In the objectives is to also design the evaluation tools that would assess its effectiveness into shaping children's environmental behaviors.

2. CASE STUDY: PROJECT SKYROS 2016

The Project "Skyros 2016" following the footsteps of the prior year's similar and multi awarded program is based on a successful cooperation between two governmental organizations, the University of the Aegean and the Skyros Port Fund. The geographic area that talks place is at the Linaria Port of Skyros Island, a boutique port that has been assessed as the best one of its category in Greece.

This year's program, Skyros 2016, similar to the last year's one, consists of a group of researchers from the Research Center of Environmental Communication and Education of the University of the Aegean, that aims to best implement a comprehensive environmental campaign focusing at disseminating information and raising environmental awareness. It includes environmental campaigns targeted at citizens, tourists, boat passengers and children, providing printed information about the biodiversity of Skyros. A Tourism Observatory has been set-up as well as an environmental camp. The environmental activities include overseeing that the Linaria Port is clean and well taken care of. Various outdoor activities in collaboration with the Port Fund of Skyros are going to be organized in order to attract residents and visitors environmental interest.

2.1 Environmental summer camp

Based on a well-prepared schedule, children are going to be confronted with various environmental issues during the 6 weeks that the summer camp will last. Firstly they are going to be introduced to the unique environmental treasure of the island of Skyros, namely its biodiversity, the flora and fauna of the region, the endangered species and some of the environmental problems that the island is facing. Then they are going to learn about global environmental issues, such as food chain, biodiversity concerns, water cycle, water pollution, air pollution, endangered species, climate change, greenhouse effect, forests, forest fires, natural disasters, floods, droughts, earthquakes, litter, energy, renewable energy, non-renewable energy, recycling etc.

3. METHODOLOGY

The research area is the island of Skyros, and specifically the port of Linaria. The small tourist port of Linaria is considered a key port, with a high tourist interest. In the last ten years, it has generated lots of attention and is presented as the most complete and friendly public port in the country, with arrivals in the tourist haven, showing an increase of 479% [20].

The tourist port of Linaria has adopted a new way of sustainable approach to the management of its environmental impact, without spending lot of its limited financial resources [20, 21]. For its adoption of strict environmental standards, the Linaria Port has been awarded a silver award in the Management of Solid and Liquid Waste. Also, a series of innovative measures, such as the establishment, construction and waterways, the use of electric bicycles and the collaboration with the

University of the Aegean, resulted in intense public interest in the innovative activities of the small port of Linaria, at Skyros Island, increasing this way the environmental support from citizens [20].

The research sample will be local children, aged 6 to 12 years old. The data will be collected through personal interviews with each child individually. The interviews will be held before the camp starts and after its end. Two questionnaires tailored to the specific needs have been put together in order to address and assess the understanding of environmental issues. The participants' attitudes and environmental behavior would also be evaluated.

Questionnaire number one is composed of 58 questions. They were selected after an extensive literature search [22,23,24,25,26,27]. The first 4 questions inquire demographics information (e.g. gender, age, educational class). The next 30 questions will assess the children's knowledge on local environmental issues, such as local biodiversity, endangered species of their region etc., and global environmental issues as well, such as climate change, global warming, greenhouse effect, air pollution, biodiversity, water cycle, extinct species, endangered species etc. Subsequently, the next 16 question are going to assess whether or not children have environmental friendly attitude and the last 8 questions are going to give some data about their environmental behavior and their willingness to participate in activities to protect the environment or to influence the decision-makers.

The final questionnaire consists of 66 questions [22,23,24,25,26,27]. The first 5 of them will be about demographics' information (e.g. gender, age, educational class). The next 29 questions are going to assess the changes on children's knowledge on local environmental issues, such as local biodiversity, endangered species of their region etc., and global environmental issues as well, such as climate change, global warming, greenhouse phenomenon, air pollution, biodiversity, water cycle, extinct species, endangered species etc., after the participation to the summer camp and the rest 20 questions are going to evaluate the changes on their attitude. The last 12 questions are going to give data about the changes on children's environmental behavior.

Some of the teaching methods that are going to be used are lecture, brainstorming, simulation and modeling, outdoor education, field study, environmental walks and field games. This project anticipates favorable results on children's knowledge, attitudes and environmental behavior.

So, children will hopefully turn into active citizens and will eventually participate as adults in the environmental decision-making processes. They will get to rethink their preexisting views and behavior with different criteria and only then they will fully understand the environmental issues of concern [28].

Participating children will get involved in activities that will take place, preferably, outdoors, where learning is more fun and tangible, since there is a direct connection to nature. Field study, environmental walks and field games are three ways through which children will come in touch with nature. During field study, children aim to observe, calculate, analyze process and interpret the elements they gather, present their results, express their opinions and suggest actions in order to solve the problem or issues that they are studying [29].

With Field games children are going to learn how to play outdoors and experience an adventure. Also they will learn how to research and how not to lose their interest through nature. Additionally they will be taught how to interact with each other. All these ways will help them create a beautiful relationship with nature, with a higher desire for active participation in environmental issues [30].

4. DISCUSSION AND CONLUSIONS

The environmental summer camp of the project Skyros 2016 is a way to deepen in some important environmental issues that the planet is facing and to channel them to children. Through the project "Skyros 2016" and especially through the environmental camp, it is aimed to sharpen the children's' curiosity over the way the environment functions, by supporting activities tailored to:

- Transmit and foster environmental knowledge at a young age;
- Motivate to solve environmental issues;
- Increase active environmental participation at their port of Linaria, and the rest of the Island;
- Understand potential environmental consequences due to their acts;
- Come in touch with nature though all their senses.

All the activities will aim to support everyone to understand the importance of the interactive relationship between man, natural and social environment. The priorities have to do with promotion of an environmentally ethical code of behavior. The ultimate goal is to give everyone the right of environmental choice through the responsibility of rightful participation.

One of the objectives of project “Skyros 2016” is to give the spark for the creation of a new society, environmentally conscious and responsible for its acts. An environmentally sensitive society is one that has knowledge and skills to solve environmental problems. This project is an effort to make children comprehend that they are part of nature’s ecosystem. Therefore loving and protecting the environment means that they respect their own life. The process of learning is a life long process that should never stop or be interrupted for no reason [31].

References

[1] Aivazidi M., 2004. Research of knowledge and attitudes of environmental educators of West Attica referring the environment. Athens: Athens University of Economics, Statistics Department, Athens (in Greek).

[2] Skanavis C., 2004, *Environment and Community*, 1st Edition, Published by Kalidoskopio, Athens.

[3] Sterling S., Cooper G., 1992. *In Touch: Environmental Education for Europe*, WWF HB

[4] UNESCO, 1978. *The Tbilisi Declaration Intergovernmental Conference on Environmental Education*. 14 - 26 October.

[5] Tahir F., 1997. *Adult education and the environment in Pakistan*

[6] Tilden F., 1977. *Interpreting Our Heritage*, 3rd Edition. University of North Carolina Press, Chapel Hill. USA.

[7] Arslan S., 2012. The Influence of Environment Education on Critical Thinking and Environmental Attitude. *Procedia - Social and Behavioral Sciences*, **55**, 902–909.

[8] Skanavis C., Matsinos G.Y., Petreniti V., 2004. Environmental education potential for Greek ecotourism, *International Journal of Environmental Studies*, **61(6),** 735-745.

[9] Kiss G., 2014. Why Should the Public Participate in Environmental Decision-Making? Theoretical Arguments for Public Participation, *Periodica Polytechnica*, **22(1),** 13-20.

[10] Karakitapolu E.B., 2015. *Public participation in EIA process of small hydro power plants (HES) in Turkey*, Swedish University of Agricultural Sciences, Department of Urban and Rural Development, Master’s Thesis, 30 HEC, Environmental Communication and Management- Master’s Programme, Uppsala

[11] Pollaki S. P., Skanavis C., 2015, Environmental Education in Action: The Case Study of WWF “School Program” in Greece, Innovation in Environmental Education: ICT and intergenerational Learning, *International Conference Proceedings*, 24- 25September 2015 Firenze, Italy.

[12] Okur-Berberoglu E., Ozdilek H.G., Yalcin- Ozdilek S., Eryaman M. Y., 2014. The Short Term Effectiveness of an Outdoor Environmental Education on Environmental Awareness and Sensitivity of In-service Teachers, *International Electronic Journal of Environmental Education*, **5 (1),** 1-20.

[13] Stevenson R. B., 2007. Schooling and environmental education: Contradictions in purpose and practice. *Environmental Education Research*, **13(2),** 139-153.

[14] Storksdieck M., Ellenbogen K., Heimlich J. E., 2005. Changing minds? Reassessing outcomes in free-choice environmental education. *Environmental Education Research*, **11(3),** 353-369.

[15] Hadlock T. D., Beckwith J. A., 2002. Providing Incentives for Endangered Species Recovery. *Human Dimensions of Wildlife*, **7(3),** 197-213.

[16] Kassas M., 2002. Environmental Education: Biodiversity. *The Environmentalist*, **22(4),** 345-351.

[17] Dori Y. J., Herscovitz O., 1999. Question-posing capability as an alternative evaluation method: analysis of an environmental case study. *Journal of Research in Science Education*, **36 (4),** 411- 430.

[18] Ford P., 1986. *Outdoor education: Definition and philosophy*. ERIC Publications; ERIC Digests in Full Text ERIC Clearing house. http://www.eric.ed.gov/PDFS/ED267941.pdf.

[19] Okur-Berberoglu E., Yalcin- Ozdilek S., Eryaman M. Y., Uygun S., Edizer Z. C., 2013. Effectiveness of an Ecopedagogy Based Outdoor Environmental Education Program on Environmental Awareness: Canakkale (Gallipoli), *International Journal for Research and Development in Environmental Education*, **2(2),** 1-16.

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[20] Antonopoulos K., Skanavis C., Plaka V., 2015, Exploiting further potential of Linaria Port-Skyros: From Vision to Realization, Conference Paper: *First Hellenic Conference on Marinas*, January 2015 At Athens, Greece (in Greek).
[21] Kuznetsov A., Dinwoodie J., Gibbs D., Sansom M., Knowles H., 2015. Towards a sustainability management system for smaller ports. *Marine Policy*, **54**, 59-68.
[22] Murphy T., 2004. *A survey of adult environmental knowledge, attitudes and behavior*. Minnesota Report Card on Environmental Literacy, Minnesota Office of Environmental Assistance, p.94.
[23] Alaydin E., Demirel G., Altin S., Altin A., 2014. Environmental Knowledge of Primary School Students: Zonguldak (Turkey) Example, *Procedia - Social and Behavioral Sciences*, **141**, 1150 – 115.
[24] http://kpe-kastor.kas.sch.gr/climate_change/index.htm (Environmental Education Center of Kastoria, 2016, 99 Questions on Climate Change and Related Issues, Accessed March 1st, 2016)
[25] http://2gym-evosm.thess.sch.gr/drupal/?q=el/node/185 (2nd Highschool of Evosmos, 2011, Questionnaire for the Environment, Accessed: March 1st, 2016)
[26] Simpson B., 1998, Environmental Awareness Survey, *Global Issues in Language Education*, **30**, 12 - 14 [reprinted by permission from Green Teacher Magazine, Issue 27 (p. 10)], Available at: http://gilesig.org/30Sur.htm
[27] Mrema K., 2008, An assessment of students' environmental attitudes and behaviors and the effectiveness of their school recycling programs, Dalhousie University, School of Resource and Environmental Studies, Halifax, NS, p.54 Avaliable at: http://www.dal.ca/content/dam/dalhousie/pdf/science/environmental-science-program/Honours %20Theses/Karen_Mrema.pdf, accessed March 1st, 2016.
[28] Georgopoulos A., Tsaliki E., 1993. *Environmental Education. Principles-Philosophy, Methodology, Games and Exercises*. Gutenberg, Athens. (in Greek)
[29] Marcinkowski T.J., Volk T.L., Hungerford H.R., 1990. *An Environmental Education Approach to the Training of Middle Level Teachers: A Prototype Programme*, UNESCO: 178.
[30] Zachariou A., Georgiou W., 2012. *Guide Programme Implemetation Studies Environmental Training-Education For Sustainable Development For Teachers of Primary Level*.
[31] Habibe A, 2014. Learning Environments for Children in Outdoor Spaces .*Procedia - Social and Behavioral Sciences*, **141**, 846 – 853

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Assessment of teachers' knowledge, training, perception and participation in environmental education in a Greek Island

K. M. Ntaiou*, C. Oursouzidou, C. Skanavis, A. Kounani

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
*Corresponding author: Email: env12061@env.aegean.gr

Abstract

In our days, it is a fact that Environmental Education (EE) projects in Greek schools face many organizational and institutional problems, although they have been introduced into the Greek educational system, almost three decades ago. This survey elaborates on the practices of EE that educators use in Greece, through a case study, which would take place at Skyros Island. A thorough literature review took place and the concept of civic ecology was compared to the outmost goal of EE. The research was carried among teachers at Skyros island schools. The methodology used was interviews, based on questions that extrapolated information on teachers' knowledge, attitudes and behavior on environmental issues. Furthermore, the teachers' personal perception on the validity of the on going environmental education school projects was assessed. Substantially, this research focuses on educators' opinions on EE and their willingness to participate in environmental projects.

Keywords: educators; environmental education practices; Skyros Island; Greece

1. INTRODUCTION

The global environmental degradation, caused by human activities, is increasing rapidly. However, environmental issues such as climate change, global warming, sea level rise, air pollution etc., affect both developed and developing countries. Environmental degradation is considered to be a very difficult task to deal with [3]. In order to stop the progress of degradation and find solutions to environmental threats, an optimal and sustainable relationship between human race and the environment must be built. To prevent further damage to the natural ecosystem, it would be necessary to produce environmental stewards capable of making knowledgeable and conscientious decisions regarding the environment [21]. Consequently, the education of the communities is the most effective way to achieve this target [1]. Children, as the future generation of decision makers, should receive proper education to prevent further environmental damage [7].

1.1 Environmental Education

Environmental Education (EE) is a process that provides the chance and the opportunity to individuals to learn about the environmental issues the planet is facing worldwide. It enables active participation of those who wish to participate in the solution of environmental problems. EE introduces participants to measures that could improve the environmental quality. Consequently, people understand in depth the environmental issues and exercise their skills into making informed and responsible decisions [4][5]. Environmental education is a form of education that does not confine itself to simple transmission of fragmentary knowledge, but takes the environment as a multifaceted, complex and interactive system [23].

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The main goal of EE is to create a world population well informed, conscious and concerned about the environmental issues. EE through the acquired knowledge, skills, attitudes, motivation and commitment to work individually and collectively towards solutions of current environmental problems and prevention of new ones gives to participants the sense of empowerment. Recently, many researchers argued that the most important component of EE is considered to be the Environmental Literacy (EL). Primarily, the EL was defined as the ability to perceive and interpret the relative quality of environmental systems and to take appropriate measures to maintain, restore or improve the status of those systems. The EL seeks specific configuration of personal values, attitudes and behaviors [23]. Researchers identified that environmental education is based on acquisition of environmental knowledge, environmental attitudes, environmental behavior, and environmental concern [20].

The EE is crucial in the support of individuals and especially children who operate based on critical understanding skills. Environmental Education is the key to knowledge transmission and to creation of experiences that turn children's beliefs, attitudes and behavior into a more environmentally friendly way of living [6]. Also, through EE the children are not only learning the fundamentals about the environment, but are also learning how to inseminate this information to their families, influencing this way household behavior [2]. A number of educational characteristics unique to EE blend well with recent educational trends: critical thinking, student empowerment, students/ researchers, place-based education, and diversity. Due to the controversial nature of environmental issues, environmental education promotes critical thinking at all times [8]. Usually EE is experienced in the formal educational system; however, it has been instrumental in informal and non-formal educational systems when promotion of responsible environmental behavior is at stake [23].

Environmental educators' role in the processes of EE is well defined. Such educators must be fully aware of the potential benefits of EE. Also they must have the required knowledge and regularly be updated on the developments of environmental sciences, be responsible and able to leverage information and technology while having the ability to design an EE program tailored to the needs of the ones they are going to deliver it to.

1.2 Environmental education for educators

In order to enhance overall the environmental educational goals, involved teachers should consider ways to increase environmental literacy. Teachers must attend pre service seminars in order to learn how to boost "environmental sensitivity", ecological knowledge, environmental emotion (attitudes), issue and action skills, verbal commitment (willingness to act), and actual commitment (behavior), within the student groups they deal with [32].

A few years ago, McKeown-Ice (2000), in order to explore why EE was not being more effectively integrated into the curricula, conducted a survey of institutions of higher learning offering teacher-preparation programs. This research identified several important barriers, such as lack of mandates from accrediting bodies to include EE in the teacher preparation curriculum, lack of correlation between EE and state and national standards and lack of faculty with content expertise, interest, or commitment to EE [17][8].

1.3 Environmental education programs

The students' learning is enhanced, on the one hand, but also becomes more effective, on the other hand, in instilling an intrinsic value of nature, with practical and comprehensive environmental activities outside the classroom [2].

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In the formal environmental education in Greek schools the environmental issues are dispersed in the outline of almost all the subjects taught into schools [19]. The objectives of the different courses in the schools of primary and secondary education mandate a specific allocation of time on relevant environmental education issues. It has been found that this environmental education component of the Greek schools curricula covers almost every issue of interest and its extent is larger than in most of the other states of the European Union [14]. The incorporation of EE in formal education has enabled the connection of the subjects taught in the schools to the environmental issues of interest in our days. The interdisciplinary nature of EE requires that knowledge is derived from various disciplines. EE has the potential to enhance critical, creative and comprehensive thinking and results into problem solving skills.

1.4 Civic Ecology

Civic ecology is a science that reflects the work of the Resilience Alliance scholars, who examine the role of linked ecological and social factors (including social capital and biodiversity) in a system's ability to sustain itself in the face of change. Civic ecology practices, defined as "local environmental stewards hip actions taken to enhance the green infrastructure and community well-being of urban and other human-dominated systems"[9]. Further, civic ecology practices represent instances of local stewardship where knowledge is co-produced by practitioners and scientists. Civic ecology practices provide opportunities for learning among both adult practitioners and youth who engage in such practices through after-school and summer programs [24][13]. Civic ecology education refers to the learning and to the social and ecological outcomes that occur when youth and others become engaged in civic ecology practices [19][12]. Because civic ecology education involves integration of novice learners into communities of more experienced civic ecologists, socio-cultural theories that emphasize learning as participation in communities of practice are relevant [29] [11].

The purpose of the present survey was to give information about the teachers' knowledge on environmental issues, coupled to their perceptions about EE programs and their own training as environmental educators. This case study research took place at Skyros Island. Teachers have a very important role in EE, making their environmental training vital to the promotion of responsible environmental behavior of the student body. Civic ecology practices, if educators are familiar with, in a small geographic area like Skyros Island, can magnify the benefits of EE. The teachers' personal perception on the validity of the ongoing environmental education school projects and their opinions on EE were recorded. Finally the educators' willingness to participate in environmental projects was also investigated.

2. MATERIALS AND METHODS

2.1 Research Area

The research included the primary and secondary schools at Skyros Island in Greece. A sample of teachers, from these schools, was the one that participated this research project. Skyros Island is the southernmost island of the Sporades Group of islands, of Aegean Sea. It is located east of Euboea. It is the largest island of the Sporades (210 km^2), with a population of about 3500 residents [33].

There are three schools at the Island of Skyros: one elementary and two schools in the secondary school system. In the primary level, 23 teachers are employed for a total of 202 students. The secondary system includes one junior school with 7 teachers and 79 students and one high school with 9 teachers and 67 students. Regarding the EE at the primary school system, the students of the 3rd, 4th, 5th and 6th grades are specifically taught the subject "Studying the Environment".

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At the secondary school system there is no specific environmental subject that is being presented as a course, students get environmental knowledge from the relevant courses they are enrolled to. Concerning environmental programs, the junior high runs a sustainable development program for ninth grade students. The high school had been involved in a program about the development of a municipal orchard.

2.2 Research Instruments

The data, supplied below, were collected in January 2016, through personal interviews with the participating educators of primary and secondary education levels. All interviewers were asked the same sets of questions, in the same order. The questions utilized at the interview, had been used before in other similar research projects [25][10][26][27][28][30][31], adjusted though to the peculiarities of the Greek school system and the application of EE in the specific geographic area. The total number of questions was 40. The first 7 questions were about the demographics (e.g. gender, age, educational status, marital status, number of children, region of origin). The next 3 questions were about the educators' teaching experience and especially in EE. Also, they were asked 4 questions on their environmental knowledge, 3 questions about the field of EE, 2 questions about their training on EE, 4 questions about their participation in EE programs and 3 questions about the civic ecology topic. The rest 14 questions aimed to assess the educators' EE concerns and perceptions (e.g. effectiveness of the existing EE practices, programs, application, support, cooperation).

2.3 Research Sample

The total number of the teachers at Skyros Island schools was 39 individuals. Only 23 of them (15 primary school and 8 secondary school teachers) responded to the research. The 35% were males and the 65% were females, aged the majority of them (91%) between 31-50 years old and the rest (8%) were between 20 to 30 years old, and older than 50 years old. Specifically, 57% were single, 39% were married and 4% were divorced. Concerning the number of children, 64% of the educators had no children, 9% of them had 1 child and 27% had 2 children. Also the 13% of them were natives of Skyros Island and the 87% of them came from other regions (74% of them from urban areas and the rest from rural areas). Only a 26% had completed graduate studies with none of them possessing a doctorate degree. Their working experience as educators was for 61% of them, a total of 1 to 10 years, the 22% had 11 to 20 years teaching experience, and the 17% of them had a teaching service of 21 to 30 years.

3. RESULTS

3.1 Teachers knowledge and training on environmental issues

Teachers' experience in EE

Sixty percent of the island's educators responded to the present survey, representing 65% of the primary school teachers' body and 50% of the secondary one. Seventy percent of them are involved directly with teaching of environmental education.

Teachers' knowledge and training on the most serious environmental issues

This type of questions aimed to assess teachers' knowledge on environmental issues and their training as environmental educators. Figures 1 and 2 shows the results of the participants' answers, on their perception about the worst environmental problem the planet is facing, and the most serious problem Greece is experiencing currently.

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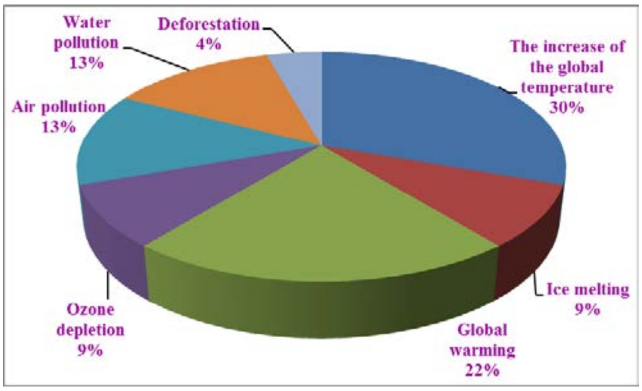


Figure 1. The worst environmental problem facing the planet, according to educators opinion

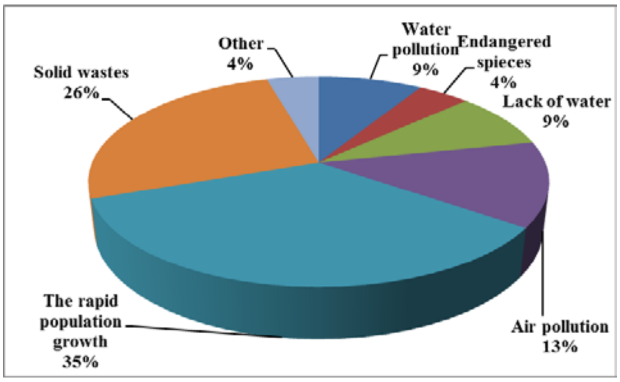


Figure 2. The most serious environmental problem educators considered Greece is experiencing currently

In Table 1, the educators' considerations on environmental statements are being presented.

Teachers' knowledge about Civic Ecology

The findings showed that the 68% of respondents were not familiar with the term "Civic Ecology". Thy all agreed that Civic Ecology practices referred to locals being involved in environmental stewardship actions. Sixty percent of the teachers said that Civic Ecology practices could provide opportunities for learning among youth, through school and summer programs, and the rest replied that it was only for adult practitioners.

3.2 Teachers' perception on the on going EE school projects

Half of them had taken part in EE programs and a percentage of 36% had created themselves an EE program. A 23% of all participants had created 1 program, 9% of them 2 programs and 7 programs were delivered by the 4% of them. The 74% of the educators believed that their own personal environmental views were being expressed in their environmental programs. Seventy percent of them answered that they were not satisfied with the number of EE projects offered to their school.

3.3 Teachers' opinions on EE

All educators (100%) thought that Environmental Education promotes environmentally friendly attitudes and behaviors. The majority of the participants (91%) considered environmental education as important as any other subject taught in school. Figure 3 shows, which benefit is perceived by teachers as the most important one gained from EE processes. A percentage of 20% of the educators were not satisfied with the effectiveness of EE practices, 50% of the educators were moderately satisfied and 30% of them were totally satisfied. Half of them were satisfied with the existing EE in Skyros Island. Almost all of them (95%) agreed with the idea of moving away from the traditional way of teaching about the environment. Only 10% of educators considered the level of EE as satisfactory. All educators (100%) thought that cooperation among teachers and school administrators is necessary for delivering the full potential of EE.

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Table 1. Responses to environmental statements

We are approaching the limit of the number of people the Earth can support.	strongly disagree	5%
	disagree	40%
	agree	40%
	strongly agree	15%
Humans have the right to modify the natural environment to suit their needs.	strongly disagree	22%
	disagree	43%
	agree	26%
	strongly agree	9%
When humans interfere with nature it often produces disastrous consequences.	strongly disagree	0%
	disagree	18%
	agree	60%
	strongly agree	22%
Science and technology can overcome any environmental problem.	strongly disagree	13%
	disagree	48%
	agree	34%
	strongly agree	5%
Humans are severely abusing the environment	strongly disagree	0%
	disagree	0%
	agree	61%
	strongly agree	39%
Plants and animals have as much right as humans to existence.	strongly disagree	0%
	disagree	4%
	agree	61%
	strongly agree	5%
The so-called "ecological crisis" facing humankind has been greatly exaggerated.	strongly disagree	17%
	disagree	53%
	agree	22%
	strongly agree	8%
Humans were meant to rule over the rest of nature	strongly disagree	26%
	disagree	48%
	agree	26%
	strongly agree	0%
Maintaining economic growth is more important than protecting the natural environment	strongly disagree	52%
	disagree	35%
	agree	9%
	strongly agree	4%
If things continue on their present course, we will soon experience a major ecological catastrophe.	strongly disagree	9%
	disagree	9%
	agree	52 %
	strongly agree	30 %

Most educators (96%) categorize environmental education as science. A percentage of 91% of educators reported the outdoor EE activities as a more effective teaching approach. Regarding the institutional framework mechanism, 58% of the educators found it unsatisfying, 21% of them stated that it was moderately satisfying and 21% of the educators found it satisfying.

Figure 4 shows the educators' experience on how the Greek state addresses the issue of EE.

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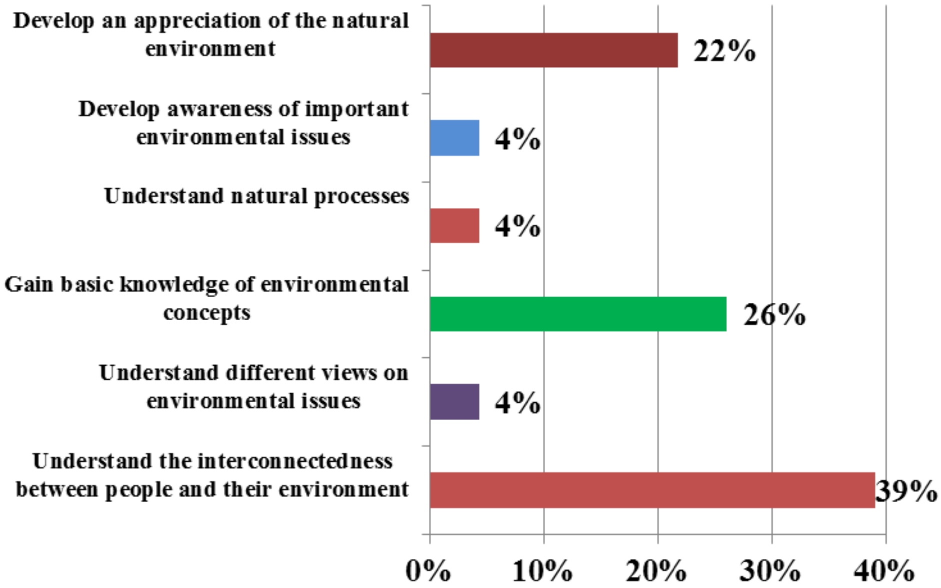


Figure 3. The most important benefits of EE that were perceived by educators

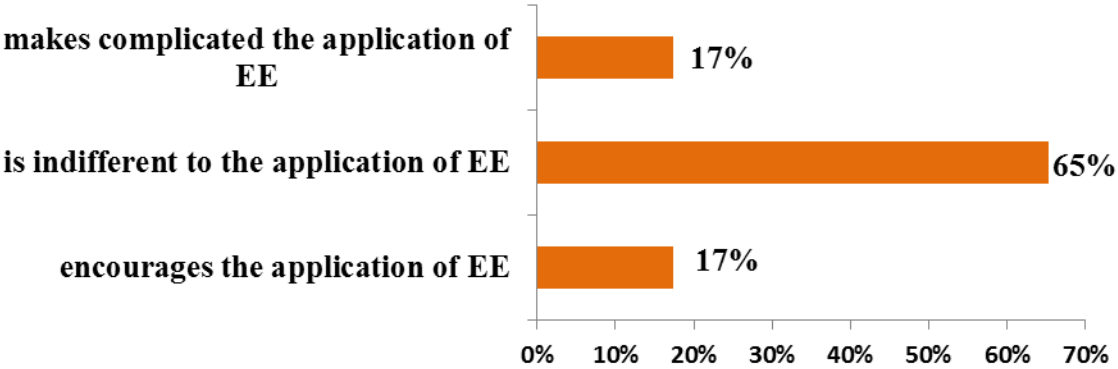


Figure 4. Educators' considerations in how the Greek state adresses the issue of EE

3.4 Teachers' willingness to participate in environmental projects

Lastly, the educators were called to express their personal opinions about what they believed could encourage other teachers to practice EE. Some (26%) of them didn't answer at all. A 35% said that educators' interest in EE could take place only though appropriate in service training programs. The rest (39%) pointed out that EE interest could be increased if there is a reduction in required working hours of teachers, or having environmental organizations' assistance or if EE becomes part of the mandatory curriculum.

4. DISCUSSION AND CONCLUSIONS

Teachers' knowledge on environmental issues and training

Skanavis (2004) has underlined that the role of the educators is critical and crucial in raising awareness, in forming attitudes, in shaping environmentally friendly behaviors and in advancing the skills of the future environmental decision makers. Many researchers have pointed out the importance and the necessity for continuous and sufficient training of teachers in Environmental

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Education. They have stressed out that the effective environmental education training is the most important factor in order to contribute in the wide spread application of EE in the formal school system [16][15].

In our days, the Greek teachers are required to teach environmental issues without having the required background, knowledge or methodology even as part of their pre service training studies. Skanavis et al. (2014) concluded in their survey, that the educational responsibility for training teachers on EE is placed under the auspices of professional environmental education experts, like the ones found in the relevant university departments. It is of great importance for children to be educated by experienced environmental educators, who will give them the proper knowledge on the environmental issues of interest and will invest on their environmental awareness and willingness to actively participate in the decision making process later on in their lives as responsible citizens.

Teachers' perception on the on going EE school projects

Only half of the teachers have taken part in at least one EE in their teaching careers. Most of them are not satisfied with the number of the EE school projects that are offered in their schools. There was though recorded a weak desire to create and implement a new EE project. This is probably a consequence to the barriers they had stated related to the enforcement and support of EE both at the national and local educational levels.

Teachers' opinions on EE

Teachers think that EE promotes environmentally friendly attitudes and behaviors. Consequently EE could create environmentally conscious citizens and policy makers, who could actively participate in the environmental decision making later on in their lives. Almost all of them agreed with the idea of moving away from the traditional way of teaching about the environment and they were supporters of the outdoor EE activities as a more effective teaching approach. It was clear though that successful EE is only possible if they receive adequate training. They are not satisfied with the level of EE, but they do not seem to have the desire to change it, as they are disappointed with the institutional framework mechanism and support educational system.

Teachers' willingness to participate in environmental projects

Having the 40% of the educators not wanting to participate in this research is an indication that EE is not among their priorities. Although they consider EE as important as other subjects taught in school, the majority of them didn't seem to have the willingness to actually practice EE. Investing in time allocation, for environmental education activities, was not in their personal agenda. Regulating authorities do not stress the importance of EE in the formal education sector. It is in the teachers' discretion to participate in an EE program and the ones that were willing to do so, were few.

The interviewees in their vast majority did not have the proper training to teach EE. Apart from a few isolated cases, the rest of educators did not feel comfortable to implement an EE program, due to lack of appropriate environmental background. The participants would have delivered EE programs if they had received professional in service training, on how to implement successfully environmental education in their teaching. This is an aspect that has been neglected, by the Ministry of Education in the last years. A remote island like Skyros has an extreme need for training support from the regulating authorities. Educators who respect their role, like the ones who participated in this study, know their limits and wish to be involved in extracurricular activities only when they feel that their contribution has positive effects on their students.

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References

[1] Arslan S., 2012. The Influence of Environment Education on Critical Thinking and Environmental Attitude. *Procedia - Social and Behavioral Sciences*, **55**, 902–909.

[2] Damerell P., Howe C., Milner-Gulland E. J., 2013. Child-orientated environmental education influences adult knowledge and household behavior, *IOP Publishing Ltd Printed in the UK*, 1-6

[3] Duraiappah A., 1996. Poverty and Environmental Degradation: a Literature Review and Analysis, CREED Working Paper Series No 8, International Institute for Environment and Development, London, Institute for Environmental Studies, Amsterdam, 3-4

[4] Environmental Protection Agency, 2014a. What is environmental education?, Available at: http://www2.epa.gov/education/what-environmental-education, [Last accessed: 2 Feb 2016]

[5] Environmental Protection Agency, 2014b. What is sustainability?, Available at: http://www.epa.gov/sustainability/basicinfo.htm. [Last accessed: 14 March 2016]

[6] Frantz C., Mayer F.S., 2014. The importance of connection to nature in assessing environmental education programs. *Studies in Educational Evaluation*, **41**: 85–89.

[7] Giannoulis C., Skanavis C., Karapatsiou E., 2014. Environmental Awareness: Environmental Accidents as an Example to be avoided. A Summative International Analysis, *Studies in Media and Communication,* **2(1);** June 2014, ISSN 2325-8071 E-ISSN 2325-808X Published by Redfame Publishing, URL: http://smc.redfame.com

[8] Hill R.A., 2016. Real World Connections: A Case for Integrating Environmental Education into Preservice Teacher Education, *Journal of Research in Innovative Teaching*, **9(1),** 70-72

[9] Krasny M. E., Silva P., Barr C., Golshani Z., Lee E., Ligas R., Mosher E., Reynosa A., 2015. Civic ecology practices: insights from practice theory, *Ecology and Society*, **20(2),** 12

[10] Krasny E.M., Russ A., Tidball G.K., Elmqvist T., 2014. Civic ecology practices: Participatory approaches to generating and measuring ecosystem services in cities, *Ecosystem Services*, **7**, 177–186

[11] Krasny M. E., Tidball K. G., 2010. Civic Ecology: Linking Social and Ecological Approaches in Extension, *Journal of Extension*, **48(1)**, 1-5

[12] Papaspiliou K., Skanavis C., Giannoulis C., 2014. Civic Ecology Education and Resilient Societies: a Survey of Forest Fires in Greece, *Journal of Education and Training Studies*, **2(2)**, 48-57

[13] Krasny M.E. and Tidball K.G., 2012. Civic Ecology: A pathway for Earth Stewardship in cities, *Frontiers in Ecology and the Environment*, **10(5),** 267-273

[14] Michaelides P. G., 2005. *Environmental Education in the Greek Schools: Topics and Issues in Education*, volume in Honor of Byron G. Massialas, Editors: M. Kassotakis, G. Flouris. Atrapos Publishers, Athens, 485-608

[15] Michaelides P., Kimionis G., Charalambidou F., 2002. The Participation of Pupils in Environmental Awareness Activities, in *"3rd Pan-Hellenic Congress in Didactics of Natural Sciences and Application of New Technologies in the Education" Rethymno* 9-11/5/2002, 108.

[16] Michaelides P., Kimionis G., 2000. *Fifteen Years of Environmental Education in the Prefecture Rethymno,* First Assessment, Conclusion and Reflections on the Future, in Mpagakis, G., (ed), "Optional Educational Programs in the School Education, Metechmio publ, Athens, 350-358.(in Greek)

[17] McKeown-Ice R., 2000. Environmental education in the United States: A survey of preservice teacher education programs, The *Journal of Environmental Education*, **32(1),** 4–11.

[18] Krasny, M.E., Tidball, K.G, 2009. Community gardens as contexts for science, stewardship, and advocacy learning: the Garden Mosaics example. Invited Submission to: Special Issue on community gardens and pollination. Cities and the Environment 2(1):8. http://digitalcommons.lmu.edu/cate/vol2/iss1/8/

[19] Pollaki S. P., Skanavis C., 2015. Environmental Education in Action: The Case Study of WWF "School Program" in Greece, Innovation in Environmental Education: ICT and intergenerational Learning, International conference proceedings, Firenze 24-25 September.

[20] Saribas D., Teksoz G., Ertepinar H., 2014. The relationship between environmental literacy and self-efficacy beliefs toward environmental education, *Procedia - Social and Behavioral Sciences*, **116**, 3664 – 3668

[21] Skanavis C., Manolas E., 2015. School Gardens and Ecovillages: Innovative Civic Ecology Educational Approaches at Schools and Universities, *Springer International Publishing Switzerland*, 559-570

[22] Skanavis C., Giannoulis C. and Skanavis V., 2014. The Significance of the environmental communication for the renewable energy governance scenario: Who decides for whom, in: Michalena E, Hills J.M. (Eds.) Renewable Energy (RE) Governance: Complexities and Challenges" Lecture Notes in Energy, *Springer,* London, 351-362.

[23] Skanavis C., 2004. *Environment and Community,* Published by Kalidoskopio, Athens, p.246

[24] Kudryavtsev A., Krasny M.E., 2012. Urban Environmental Education: Preliminary Literature Review (Document number CEL-2012-1), Cornell University Civic Ecology Lab, Ithaca, NY.

[25] Kearney, A., 1999. Teacher Perspectives on Environmental Education and School Improvement, Model Links "Environmental Education and School Improvement" Program, The Evergreen Center for Educational Improvement Evergreen State College, 15- 30

Editors: A. Kungolos, C. Christodoulatos, A. Koutsospyros,
C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

[26] Kimionis G., Michaelides P.G., 2005. Environmental Education in Greek Schools: The Viewpoint of the Local Coordinators, *2nd International Conference on Hands on Science Hsci 2005 – Science in a Changing Education*, July 13-16, The University of Crete campus, Rethimno, Greece, 197-201
[27] Powers A.L., 2004. Teacher Preparation for Environmental Education: Faculty Perspectives on the Infusion of Environmental Education Into Preservice Methods Courses, *The Journal of Environmental Education*, **35(3)**, 3-11
[28] Robertson C.L., Krugly-Smolska E., 1997. Gaps between Advocated Practices and Teaching Realities in Environmental Education, *Carfax Publishing Ltd*, **3(3),** 311-321
[29] Wenger E.C., McDermott R. and Snyder W.C., 2002. *Cultivating Communities of Practice: A Guide to Managing Knowledge*, Harvard Business School Press, Cambridge, USA, p.304 \(ISBN 1-5781-330-8)
[30] Legault L. and Pelletier L.G., 2000. Impact of an environmental education program on students' and parents' attitudes, motivation and behaviors, *Canadian Journal of Behavioral Science*, **32(4),** 243-250
[31] Simpson B., 1998. Environmental Awareness Survey, *Global Issues in Language Education*, **30**, 12-14
[32] McBeth W. and Volk T. (2010). The national environmental literacy project: A baseline study of middle grade students in the United States. *Journal of Environmental Education*, **41(1),** 55-67. doi: 10.1080/00958960903210031
[33] Antonopoulos K., Skanavis C., Plaka Valentina, 2015, Exploiting further potential of Linaria Port-Skyros: From Vision to Realization, Conference Paper, January 2015, Conference: First Hellenic Conference on Marinas, At Athens, Greece (in Greek)

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Investigation of the interview as a measuring tool for environmental illiteracy in Greece

J. Barota, H. Giannakopoulou, C. Skanavis*

Department of Environment, University of the Aegean, University Hill, 81100, Mytilene, Greece.
*Corresponding author: Email: cskanav@aegean.gr

Abstract

The purpose of this study was the investigation of the effectiveness of interview as a measuring tool of the environmental illiteracy. A pilot conduction of interviews was made in a sample of twenty children in the first and second class of High school in central Evia. The structure of interview was shaped after having reviewed the relevant literature and other questioners that have been used occasionally for the environment literacy. A part from the introductory demographical questions the main body of the interview investigated the children's environmental sensitivity consisting of questions about a) their basic knowledge about the environment, b) their attitudes towards it, c) any possible actions they engaged in about the environment. The results of the survey highlighted the big luck of knowledge and of proper models on environmental education. The terminations showed that, half of the children separate some of their waste into recyclable and non recyclable ones. The children were ready to save energy and water as well as urge people's recycling awareness. Only ¼ of the students had discussed with their parents on the solutions of environmental issues. The responses underline the children's desire to take up actions about the environment but at the same time their inertial about it, which may be the result of most parents' indifference to be active and environmentally aware. As the conduction of the study was pilot a more extensive research is proposed to be done in the future. Given the students preference on the interview as a measuring tool, the last appears to be a very useful mean for research in the future, as other methods were considered to be boring and tedious according to the children's' reactions. Watch more a possible combination of methods of investigation could provide more reliable and detailed results for the critical issue of environmental illiteracy.

Keywords: environmental illiteracy; environmental education; interviews; Greek High school; environmental issues

1. INTRODUCTION

Environmental issues not only turn the world into an uninhabitable place but also threaten human existence. To cope with these issues, the activities aimed at transforming the behaviors of individuals are vital, in addition to technological advances. This is possible only through environmental education [1]. At the 2002 United Nations World Summit for Sustainable Development in Johannesburg, it was noted that sustainable development requires a long-term prospect and wide participation in policy planning and decision-making [2,3].

To provide awareness and develop an ability in young people to look at ecological subjects with more of an integrated approach, individuals must comprehend that solving an emerging problem successfully, and developing and integrating environmental perception in children at an early age must be a priority. Therefore the fundamental basics need to be taught, and ideas need to be shared and discussed within the family and at school [4].

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According to Tanaka [5], environmental knowledge can be defined as individual understanding on how environment functions; how humans interact with the environment; how environmental problems arise; and in what way these problem can be overcome. For Rohiza [6], environmental knowledge can be explained in the context of an environmental literacy component regarding the knowledge of issues related to environmental sustainability and its influence on human life.

The first step to the teaching about the environment should be first to train active and aware people about the environment and their responsibility in conserving it. Through training, students must obtain a set of values and interests in the environment and become motivated to engage in active partnership in conserving and improving the environment [7]. In fact, to train aware and responsible citizens about the environment and its problems, to provide awareness about and an eagerness to discover solutions to its problems are extremely important teaching priorities [8].

Erten [9] underlines the importance of environmental education for the protection of the environmental attitudes, values, knowledge and skills development, and eco-friendly behaviors. Moseley [10] defines environmental education as a life-long interdisciplinary approach contributing to the solution of current environmental problems with the goal of creating a world population who is responsible for the things they have done to the environment. When all definitions are taken together, environmental awareness is thought to be important, aiming at encouraging people to actively participate in the solution of problems as responsible individuals [11].

The concept of environmental literacy was firstly defined by Charles E. Roth in 1968 as an individual's environmental knowledge and awareness level. Morrone indicates that an environmentally literate individual should have a basic and deep scientific background, converting knowledge into action with increased environmental values, attitudes and skills [12].

Roth [13] defined environmental literacy as "the capacity to perceive and interpret the relative health of environmental systems and take appropriate action to maintain, restore, or improve the health of those systems". They found that environmental knowledge was correlated with environmental concerns and perceptions of environmental behavior.

There is a profound, but subtle, distinction between environmental education and environmental literacy. While environmental education is process based, the goals of environmental literacy are more outcomes based. Environmental literacy is the understanding of the interactions between natural systems and human social systems [14]. The working definition of an environmentally literate person is one who uses critical thinking, problem solving, and effective decision-making skills to weigh all sides of an environmental issue [15].

In Greece, Environmental Education Centers, which were introduced in 1993, could be utilized in the promotion of environmental literacy of the visiting students. Furthermore, the establishment of school gardens can be planned as an ecological field for students who have no chance to attend ecological education programs, and extra-curricular environmental activities can also be organized in these places [16]. The Laboratory of Environmental Education and Communication, in the Department of Environmental Studies at the University of the Aegean, has studied several groups of individuals with a broad spectrum of educational, career and age characteristics – all of whom are involved with environmental education in one way or another, or are interested in environmental protection, in order to profile their environmental interests [17].

Children cannot be taught about the future environmental problems yet to happen. However, they can be helped and encouraged in: generating their mental abilities which identify and foresee problems related to the habitat, gathering information about relevant subjects from the field, providing problem-solving opportunities and making reasonable decisions with these pieces of information and in turn, solving environmental problems [18].

Teachers play an important role in ensuring their students get adequate knowledge to preserve and conserve the environment. However, a study by Che Kalbi [19] and Khor [20] showed that teachers' level of knowledge on the environment is between moderate to high.

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Young people can benefit from personal experiences and can develop skills in many areas: cultural, biogeographic knowledge of underground processes, and the participant's own senses [21].

Another study [22] showed that affective variables seemed to have greater influence on students' behaviors, emotional bonding, for example, and sensitivity toward nature, traits that may have influenced their environmental literacy.

2. RESEARCH AND RESULTS

The purpose of this study was to investigate a tool (interview) used to examine the current situation in Greece and the Greek schools on environmental education. The pilot procedure in our research included 20 students who studied in the first and the secondary class of Greek High School, in order to investigate the effectiveness of this tool. For creating of the frame of the interview, questions from other questionnaires and interviews were used to Greek reality and the particularities of the respondents. This interview was standardized and structured. It was divided into six main axes with questions not only of demographic interest, but also questions about the environment, their knowledge and their sensibilities. In this way, the investigation has established a relationship of trust between the two parties. This relationship is necessary so that the findings may be true, rich and quite able to expand the research.

Analyzing the results of the interviews, the first set of questions give us demographic information of the respondents such as their gender (60% of them were boys), their age (65% of them were students of the seventh grade and 35% of them were students of the second year of secondary school). Subsequently, they were asked whether they recycle and what items they use (55% responded negatively). Also, 65% of the students have already participated in an environmental program, while the 75% would like to participate in such an occasion. The 75% believe that the greatest environmental problem is the green-house effect (global warming), while the 30% believe that the most important environmental issue is the ozone hole. Moreover, concerning the question as to who is responsibility for pollution, the majority (70%) chose the factories, 25% chose the state and 5% chose the households. As for the question about which of their daily habits could contribute to environmental protection, 25% of the students replied that an effective way is saving water, 20% of them selected energy saving and 10% mentioned several activities like reforestation and cleaning the beaches.

The remaining 45% of the students thought that recycling is another effective way. Then, to the question as to when a material is called recyclable, 85% of the students answered correctly, 10% chose the wrong answer and 5% gave no answer. Furthermore, 50% of the respondents knew about composting. In addition, to the next question about which of the items that followed was a predator/prey relationship, three indicative answers were given. Eighty percent of the students answered correctly (a robin eats a worm). Fifteen percent of them gave a wrong answer (a fish eats aquatic plants) and the remaining 5% chose the answer when a flea bites a dog, which was wrong too. Then the students were asked about which the original energy source for all of living beings is. In this question 10% of the students gave a wrong answer (water) whereas the rest of them answered correctly (the sun).

Another question with overwhelming results was the one about where the majority of oxygen in the atmosphere comes from. Ninety five percent of the respondents gave the correct answer (from the plants) while only 5% of them gave the wrong one (from the soil). In addition, the results to the question as to which of the items that followed were parts of the water cycle were remarkable. More specifically, 95% of the students answered correctly (evaporating) and only 5% of them answered wrongly (tides of the oceans).

In the next chapter of questions which was about the thoughts of children concerning the environment, 100% of them answered that they are willing to save energy by decreasing the use of

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air conditioning. In addition, when they were asked whether they are willing to use less water when they take a bath in order to save water, 100% of them answered positively. Also, 100% of the respondents gave an affirmative reply when they were asked if they would be willing to walk more in order to reduce pollution. Likewise, 95% of them answered positively to the proposal about asking other people to start recycling.

Furthermore, the students were asked about what they do for the environment. More specifically, they were asked if they had already had a discussion with their parents on how they could solve environment problems, to which 75% of them answered negatively. Also, 60% of the respondents stated that they do not turn off the faucet when they brush their teeth (to save water) nor do they switch off the light when they don't need it. Apart from that, 75% of them had never asked their family to recycle some of the items they use.

The last section refers to the environmental awareness of the children who participated in this research. As far as this matter is concerned, 70% of the participants had a moderate level of environmental awareness, 25% of them had quite enough and 5% of them had a low level of awareness. Also, to the question about how often they go on vacation with their family, only 15% of them gave a positive answer. Likewise, only 20% of the students have gone camping. In addition, when they were asked whether they like to read environmental books or magazines, only 25% of them gave a positive answer. Lastly, 70% of the participants said that they had a teacher or a mentor as a role model when it came to environmental consciousness.

3. DISCUSSION AND CONCLUSIONS

The findings of this study showed that generally there were no signs of student stumping in the interview, with few exceptions. This interview offers valuable elements which we did not have the opportunity to have access to through other ways of research. It is a kind of insight into the inner world of students.

The children's knowledge concerning various ecological issues is satisfactory. As a result, a large number of questions was answered correctly. The majority of children knows where most of the oxygen in the atmosphere comes from and what the water cycle is. The above shows that schools aim to create a new environmental culture through the knowledge and behaviors that support the correct sustainable society as well as the well-being of each one of its individuals. In recent years, especially after the Rio Summit in 1992 and the Johannesburg Earth Summit in 2002, the idea of an Education for Sustainable Development was crystallized.

The Education for Sustainable Development gives a new vision and a different educational approach that will enable students to understand the world in which they live better as well as be aware of the interface problems such as over- consumption, depletion of natural resources, urban decline and environmental degradation, which will help them cope with the complexity of reality [2].

Through courses of "Interdisciplinary Activities, Development Guide Environmental Education" and "Geography", students of the first class of high school get impulses on matters concerning the environment. They distinguish the natural from the human environment and understand the forms and causes of pollution as well as the degradation of the environment. Moreover, they realize the interdependence of natural resources and human activities, the land use and bearing capacity and recognize the value of sustainability. Finally, they can determine the precise meaning of the terms "Quality of life" and "Land use" [23].

Students of the second class of High school who are taught "Interdisciplinary Activities, Development Guide Environmental Education", "Geology-Geography" and "Chemistry" are able to indicate factors that disturb the water cycle, to describe the association of surface with groundwater, investigate the causes of abandonment or degradation of the environment as well as the cultural identity of a place at a local, national and global level. Moreover, they can predict the consequences

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of continued neglect and environmental degradation [24].

The findings of this study show that students are prepared to raise awareness on key issues concerning the ecosystem of the region and their sustainable management. Furthermore, they are informed about the dangers that threaten them and have become familiar with practices of sustainable forest management like saving energy, using less air conditioning and so on.

Regarding the questions about what respondents do for the environment, it comes as a result that they don't do what they want. Only 45% of the students do recycle at home. Of course, we must note the important role in the development of children. Parents can help their children in such a way that they establish environmentally friendly attitudes or behavior patterns, through both intentional and systematic educational interventions [25].

Highly educated people as well as younger people tend to develop friendly environmental behaviors. Also, another factor that affects the appearance of environmentally friendly behavior is gender, since women seem to react more emotionally towards environmental problems and show more interest [7].

Human impact is the main source of environmental problems while humans are also the answer to the solution of these problems [26]. The configuration formation of environmentally responsible behavior is a complex process depending on the interaction of endogenous and exogenous factors. On an individual level, behaviors are the results of the engagement of various factors which interact differently depending on the occasion each individual is found in [27]. The environmentally friendly behaviors depend mainly on a network of personal and perceptual characteristics of the individuals, such as attitudes, values, intrinsic motivation and so on. Today, we are trying to reestablish the place of humanity in nature and his relationship with it [28].

Even if we become fully aware of the whole philosophic system regarding the relationship between humans and nature, we will not manage to diminish this crisis, unless we implement the principles of this system in our educational system at an early age. More specifically the role of the teachers and educators is crucial in helping their audience to think and act critically [26]. The role of the teacher and the school should be noted for the students' attitudes [27].

Moreover, teachers must change their role and knowledge transmitters so as to become animators as well as coordinators for the pupils [27]. As a result, they will be able to interact with each other, which will give the latter the opportunity to gain the new knowledge. Furthermore, the former should give great value to the interests, ideas and expectations of the students. The design of the whole venture should be open and flexible. This attempt to explore and capture the environmental awareness of students shows that the respondents were honest. More specifically to the question that referred to the extent they were environmentally aware, the majority of the students answered "to a certain degree". When asked whether they love or hate the environment, the students went for the former. It is crucial to support students in identifying their values, so that they can envisage how these values might work out in practice. Thus, we do not advocate any specific, responsible environmental kind of behavior; rather, we promote a lifestyle according to which actions are consciously and reflectively driven by values and a vision of welfare for the world [27].

Some environmental thinkers, like John Muir, believe that if people have more opportunities to see or enjoy natural landscapes, they will be made to value and preserve these places more [29].

The individuals who have environmental consciousness can put pressure on politicians and awaken them [30]. Future approaches for environmental management and policies can be made possible by raising individuals who will be educated, aware of environmental issues and willing to apply the results of this education to their attitudes and conscious lifestyles. Considering the important role of the family in environmental education and the awareness of the child, we deem that it is necessary for parents to provide their children with appropriate personal experiences as well as a potential treatment framework through which children will construct their own mental patterns and will be led to the gradual building of a value system and the shaping of environmentally friendly attitudes.

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C. Emmanouil, C. Laspidou, Z. Mallios, D. Dermatas
ISBN: 978-960-6865-94-7

References

[1] Erten S., 2012. Türk ve Azeri öğretmen adaylarında çevre bilinci. [Environmental consciousness among Turkish and Azeri candidate teachers] *Education and Science*, ***37***(**166**), 88-100.

[2] United Nations, 2002. Report of the World Summit on Sustainable Development Johannesburg, South Africa.

[3] Skanavis C., Sarri, E., 2004. World summit on sustainable development: an environmental highlight or an environmental education letdown. *The International Journal of Sustainable Development and World Ecology*, **11**(**3**), 271–279.

[4] Moyle Kathryn, 2010. Building Inovation: *Learning with technologies*.

[5] Tanaka H., 2000. Environmental chemistry education for the 21st century. *Journal of Indian Chemical Society*. **77**, 531-538.

[6] Rohiza Jamaluddin., 2004. Pencapaian guru sains sekolah menengah dalam pernyataan tentang isu alams sekitar. Unpublished master's thesis. University Malaya.

[7] Palmer J.A., 1998. Environmental Education in the 21st Century: Theory, Practice, Progress and Promise.

[8] Veeravatnanond V., Singseewo A., 2010. A Developmental Model of Environmental Education School. *European Journal of Social Sciences*, **17**(**3**), 391 403.

[9] Erten S., 2004. Okul Öncesi Öğretmen Adaylarında Çevre Dostu Davranışların Araştırılması. *Hacettepe Üniversitesi Eğitim Fakültesi Dergisi,* **28**, 91-100.

[10] Moseley C., 2000. Teaching for Enviromental Literacy. *Clearing House* **74** (**1**), 23-25.

[11] Özdemir O., 2007. Yeni Bir Çevre Eğitimi Perspektifi: Sürdürülebilir Gelişme Amaçlı Eğitim. *Eğitim ve Bilim Dergisi*, **32** (**145**), 23-38.

[12] Kisoglu M., Gurbuz H., Sulun A., Alas A., Erkol M., 2010. Cevre Okuryazarligi ve Cevre Okuryazarligi ile Ilgili Turkiya'de Yapilan Calismalarin Degerlendirilmesi. *International Online Journal of Education Science*, **2**(**3**), 772-791.

[13] Roth C. E., 1992. Environmental literacy: its roots, evolution, and directions in the 1990s. *ERIC Clearinghouse for Science, Mathematics, and Environmental Education*. (http://www.eric.ed.gov/PDFS/ED348235.pdf)

[14] Barrett G.W., Peles J.D., Odum E.P., 1997. Transcending processes and the level-of-organization concept. *BioScience*, **47**(**8**), 531-535.

[15] McBeth William C., 1997. An Historical Description of the Development of an Instrument to Assess the Environmental Literacy of Middle School Students. Doctoral dissertation. (eds) Southern Illinois University at Carbondale, Carbondale.

[16] Erdogan M., 2011. Ekoloji Temelli Yaz Doga Egitimi Programinin Ilkogretim Ogrencilerinin Cevreye Yonelik Bilgi, Duyussal Egilimler ve Sorumlu Davranislarina Etkisi. *Kuram ve Uygulamada Egitim Bilimleri*, **11**(**4**), 2223-2237.

[17] Skanavis C., Giannoulis Chr., 2009. A training model for environmental educators and interpreters employed in Greek protected areas and ecotourism settings, 16(3), 164-176

[18] Uzunoglu S., 1996., Cevre Egitimin Amaclari, Ugrasi Alanlan ve Sorunlari. *Ekoloji*, Ekim – Kasim – Aralik Sayi, **21**, 7-12.

[19] Che Kalbi Mohd Ali, 1999. Tahap pengetahuan isu-isu alam sekitar di kalangan guru pelatih kursus diploma perguruan Malaysia semester 5 Maktab Perguruan Kota Bharu. University Malaya.

[20] Khor C. Y., 2006. Keprihatinan Alam Seitar di Kalangan Guru-guru prasekolah di pulau pinang. University putra Malaysia

[21] Smeds P., Jeronen E., Kurppa S., Vieraankivi M., 2011. Rural Camp School Eco Learn – Outdoor Education in Rural Settings. *International Journal of Environmental & Science Education*. **6**(**3**), 267-291.

ISBN: 978-960-6865-94-7

[22] Alp E., Ertepinar H., Tekkaya C., & Yilmaz A., 2008. A survey on Turkish elementary school students' environmental friendly behaviours and associated variables. *Environmental Education Research*, **14**(**2**), 129-143.
[23] UNESCO, 2002. Education for Sustainability, From Rio to Johannesburg: Lessons learnt from a decade of commitment.
[24] http://digitalschool.minedu.gov.gr (Curriculum High School Learning field "Environment and Education for sustainable development" compulsory education accessed June 5th, 2016).
[25] Poehlmann J., Dallaire D., Booker Loper A., Leslie D., Shear., 2010. Children's Contact With Their Incarcerated Parents: *Research Findings and Recommendations*, 65(6), 575–598.
[26] Bradley J. C., Waliczek T. M., Zajicek J. M., 1999. Relationship between Environmental Knowledge and Environmental Attitude of High School Students. *Journal of Environmental Education*, **30** (**3**), 17-21.
[27] Hughes J., Kwok O., 2007. Influence of Student–Teacher and Parent–Teacher Relationships on Lower Achieving Readers' Engagement and Achievement in the Primary Grades. *Journal Edu.c Phychol.*, 99(1), 39–51.
[28] UNESCO, 2002. Learning to be: A holistic and integrated approach to values education for human development: Core values and the valuing process for developing innovative practices for values education toward international understanding and a culture of peace. Bangkok.
[29] Skanavis C., Manolas E., 2014. *School Gardens and Ecovillages: Innovative Civic Ecology Educational Approaches at Schools and Universities*. Transformative Approaches to Sustainable Development at Universities. Springer International Publishing, Switzerland.
[30] Ileri R., 1998. Cevre Egitimi ve Katilimin Saglanmasi. Cevkor – Ekoloji, Temmuz – Agustos – Eylul Cilt: 7 Sayi: **28** (**3 - 9**)

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Evaluating the implementation of WWF Hellas program for a "Better Life"

S. Pollaki*, C. Skanavis

Department of Environment, University of the Aegean, University Hill, 81100 Mytilene, Lesvos Island, Greece.
*Corresponding author: Email: env10080@env.aegean.gr

Abstract

The following article refers to the current way that Environmental Education (E.E.) is being incorporated in primary schools in European countries, and specifically the Greek primary schools. It emphasizes the implementation of an alternative environmental program by the N.G.E.O. WWF Hellas. Furthermore this article refers to the role of Non Governmental Environmental Organizations (N.G.E.O.) in E.E and its evaluation. Finally it addresses how the field of Environmental Education (E.E.) has incorporated effective ways into creating responsible environmental behavior.

Keywords: environmental education; responsible environmental behavior; evaluation of environmental programs

1. INTRODUCTION

The issues of environmental instability and worldwide environmental degradation have resulted in a call for greater emphasis on environmental education (EE) in order to create and maintain optimal and sustainable relationships between the public and the environment [1]. Recognizing that human influences have the greatest impact on the environment, specific programs in governmental sectors, non-profit organizations and public schools focused on the promotion of environmental actions for children who are going to be the 'future' citizens [2].

The most effective way in order to solve the environmental problems is the education of the societies [3]. The active participation in issues involving the environment is required [4]. In our days, young students are technologically adept, but without the connection to nature, which is so important in early years, children are going to be deprived from developing an 'environmental sympathy', respect and curiosity about the natural world. Young individuals should experience the power, fragility, interconnectedness and awe of nature, so they can become environmental stewards of the future [2]. The fundamental objective behind environmental education is to foster environmental awareness in all segments of society and inculcate positive enduring behavioral changes [5]. Outdoor educational programs are generally believed to be a suitable alternative to conventional biology settings that improve participants' environmental attitudes and knowledge [2]. The purpose of nature education is to help the participants identify nature, its products and meaning by interacting with it. From this standpoint, this type of education should be carried out in real conditions in order to enhance interest for nature and relate with it [6].

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2. ENVIRONMENTAL EDUCATION (E.E.)

E.E. is considered an ongoing process, which is an integral dimension of citizen education, oriented towards knowledge acquisition, development of habits, skills, attitudes, and values formation [7]. It plays a significant role in harmonizing the relation between men and nature, providing the reorientation of economic, social and cultural variables when sustainable development is the issue of concern [8]. E.E. imparts knowledge and creates experience to change beliefs, attitudes – and most importantly – behavior [9]. The basis of teaching is to connect with the children through their own experiences [1]. This form of education could be considered “learning by doing” which is believed to be highly meaningful and therefore retained longer by the students [10]. Affective variables seemed to have greater influence on their behaviors, emotional bonding, for example, and sensitivity toward nature, traits that may have influenced their environmental literacy [11]. Studies have started to reveal that environmental concerns and the environmental fear, known as eco-phobia, relate to feelings of helplessness, which may impact children’s willingness to participate in environmentally friendly activities [12].

2.1. Environmental Education in primary school system

The educational system worldwide is charged with the vital task of encouraging students to promote responsible environmental behavior, and, furthermore, of assisting them in their advocacy [7]. Environmental education assist youth in developing mental skills, which enable young individuals to identify the environmental concerns, to collect information about the relevant issues, to take the right approach, and to solve the environmental problems [13]. Emerging environmental education components require new approaches to teaching, incorporating inquiry methods and field studies, ensuring the integration of knowledge, emotion and action, i.e., “heads, hearts and hands” [14].

2.1.1. In Greek schools

The school, in these days, cannot ignore the demands of modern society that wants man to be an active and responsible citizen based on free will [15]. As a result the ‘’Flexible Zone’’ has been implemented in schools, in which all the primary and nursery schools are obliged to execute programs and working plans, as stated in relevant educational regulations [15]. Students are not only tested on acquired knowledge, but they are encouraged to participate in relevant activities [15]. Based on national educational acts the Environmental Education is part of the pedagogical processes in both primary and secondary schools [15].

2.2. Case Study: “Better Life – economy, ecology, participation’’

The program of WWF Hellas, «Better Life - economy, ecology, participation" started in October 2013 and it is a comprehensive public information and training hub in everyday matters, providing simple and effective recommendations for all and encourages involvement in small and large acts of cooperation and solidarity. This program is developed on four themes: a) consumption, b) nutrition, c) city life, and d) energy, it is aimed at the entire society (citizens, students, teachers, etc.) in order to improve the everyday lives of Greeks and encourage them to take actions at home, the neighborhood and the city. It is approved by, the Greek Ministry of Education. WWF Hellas created this program in order to propose a new model of life by which citizens would be persuaded to reduce the ecological footprint and the heavy demand for natural resources. This program sets daily activities and it tries to prove that the environment, society and the economy are interdependent parts. It aims to promote a lifestyle different and better, since it would be based on collective action, cooperation, information, environmental education and "special missions". This program attempts to identify policy weaknesses in order to change policy at central or local level [16]. WWF Hellas under the Better Life program works with the Future Library network [17] and creates special training programs for librarians.

2.2.1. At the schools

The aim of this program is to motivate students, teachers, parents and local residents. The driving force is the school but the activities are diffused in homes, the streets and neighborhoods. WWF Hellas invites teachers and students to work with all citizens and to take actions to improve the quality of city life, home and neighborhood. The schools can sign up in the program Life Best and then they get involved with one or more topics that have been proposed (Consumption, Diet, Green City, Energy) and at three levels: school, home, neighborhood. When someone from the school signs up, he/she can see the available actions and the schools that participate in the program. With the completion of each action, every participating school has the opportunity to record the experiences of children and to upload relevant material with photos and videos to inspire others. Schools have the opportunity to communicate, to exchange views and to work together. On the website of this program there is educational material on each working topic, which provides ideas and suggestions for action, but also gives guidance on how these activities can become effective [16].

2.2.2. Data Analysis

The Better Life program of WWF Hellas has 6.725 members and it has implemented 85 actions until now, which are based on the topics of consumption, nutrition, city life, and energy. Examples of related actions are: take the green in your hands; what season is suitable to sow; what we have to do to avoid a fire; eco-driving; creating compost; garden creation in yards and gardens; reuse and creation of handmade things; cooking without wasting etc. Examples of programs are: the road of the water, green brunch, garden creation in the schoolyard, exchange, construction and corrections in order to minimize energy losses in the school buildings, etc.

2.3. NGOs as a means for effective environmental education

Environmental education is the crux of an NGO’s work. Without knowledge, there can be no action, and without action there can be no change. The students are not taught “what to think” but “how to think”, giving them skills to analyze information, make “sound” judgments and respond with solutions, ideas or new questions [18]. The interactive method (discussions and experiments) internalizes the behavior. With adequate awareness, facilitation and positive experiences in the environment, students can be encouraged to design and implement their own projects [18].

2.4. Responsible Environmental Behavior (R.E.B)

The humans live and operate, virtually without exception, in social systems that are inextricably linked to the ecological systems in which they are embedded [7]. E.E. must offer cognitive and emotional stimuli, which are concerned with the formation of values, attitudes, and—subsequently - behavior [7]. According to research projects, participation in environmental education and the belief that this education is able to foster behavioral change are closely related [19]. There are studies indicating that when the environmental education is carried out in nature with field works, it is easier for the acquired knowledge to turn into behavior and to develop positive environmental attitudes [6].

The knowledge is a necessary, however not sufficient precondition for developing pro-environmental moral norms and attitudes [20]. The main goal of environmental education should thus be to engage students with a complex toolset - containing cognitive, affective and conative elements - which foster behavioral change [19]. When people feel a sense of ownership of the goals they select, they typically try harder and longer [21].

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3. EVALUATING ENVIRONMENTAL EDUCATION SCHOOL PROGRAMS

EE is enhanced through the evaluation of its programs. Disseminating evaluation results, to a broader audience, increases even further the benefits associated with improvement of EE practices. The programs' evaluation is an attempt to measure the overall impact of the corresponding programs. Specifically evaluation refers to the systematic collection of information about the activities, characteristics, and outcomes of programs, in order to make suggestions about how the program can improve its effectiveness [22].

The evaluation of a program determines the degree to which the program contributes to the overall environmental literacy [23]. It includes ways to capture and assess unanticipated outcomes and it determines if the addressed needs were correctly identified in the initial needs assessment report [23].

Questions that should be included in an evaluation are the following [24]:

- How satisfied are the program participants?
- What are the demographics of the program participants? How did the program participants feel and which of their attitudes changed after the implementation of the program?
- Did the program increase stewardship behavior?
- What did the program participants learn from the program?
- Did the program have impacts on eco practices, biodiversity, water quality, solid waste and sustainability?

In general, evaluation results are used to help determine areas of strength and potential gaps, how a specific activity has impacted the community, how to function more effectively, to identify areas needing attention or improvement, to help clarify issues, to provide direction, to inform decision-making, to promote the program within the community, to communicate within one's own agency or organization, to fulfill funding requests, to build group visibility in the community, and to recruit other participants [23]. The assessment of the evaluation reports serves as an educational tool and directs experts into creation of new programs that will have a positive impact on the community.

4. ENVIRONMENTAL EDUCATION THEORY RELATING TO WWF HELLAS ACTIONS

The implementation of the program "Better Life - economy, ecology, participation" of WWF Hellas is fully harmonized to environmental education theory, principles and agenda.

Through the environmental education, children and adults learn and explore their environment and make smart choices for an improved everyday life by reducing their ecological footprint. Education should encourage critical thinking and be linked to personal experiences and everyday life demands. This way, through acquired knowledge and information, the configured values support environmental attitudes, which in turn result in the promotion of environmentally responsible communities.

The Better Life program proposes actions, which encourage people to deal with environmental protection and get to know nature by interacting with it (e.g. creation of gardens). The program sets small, achievable goals (e.g. festivities without wasting food), motivating this way everyone to participate, learn and act. These small but very important everyday interactions create the will to program participants to want to work harder for the environment's sake as well as their own, because they realize the importance of their own actions. The personal motivation to engage into environmental tasks comes from within us, a concept that is supported by the Self Determination Theory (SDT) [21]. The program encourages all participants to communicate and share experiences,

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difficulties in implementing the actions, tips and questions. New members of the community are constantly lured into wanting to become part of this environmental “cult”.

5. DISCUSSION - CONCLUSION

It is of paramount importance to understand children’s perspectives, since children both now and in the future will influence and be influenced by environmental issues in many ways [12]. Outdoor environments can enhance mental health of participating students, contribute to students’ intellectual and emotional development, support their environmental awareness and can give them opportunities to play and get involved in creative activities as well as connect directly with nature [2].

The "Better Life" program aims in a new type of practice, i.e., civic ecology practice. Students are introduced to significant daily issues. The program is an exploration of urban stewardship, with the goal of developing a deeper understanding of how such practices emerge, grow, and are sustained over time [25].

If citizens all over the world had been environmentally educated to actively participate in the decision-making process, we wouldn‘t need to worry about environmental disasters [7]. Responsible citizens, able to manage environmental issues and to control their own environmental destiny are the true target of the WWF Hellas program that was presented in this paper.

References

[1] Blanchet-Cohen N., Reilly R.C. 2013. Teachers’ perspectives on environmental education in multicultural contexts: Towards culturally-responsive environmental education. *Teaching and Teacher Education*, **36**, 12–22.

[2] Plaka V., Skanavis C., 2016. The feasibility of school gardens as an educational approach in Greece: a survey of Greek schools. *International Journal of Innovation and Sustainable Development,* **Vol. 10, No. 2**.

[3] Arslan S. 2012. The Influence of Environment Education on Critical Thinking and Environmental Attitude. *Procedia - Social and Behavioral Sciences*, **55**: 902–909.

[4] Krasny M.E., Silva Ph., Barr C., Golshani Z., Lee E., Ligas R., Mosher E., Reynosa A. 2015. Civic ecology practices: insights from practice theory. *Ecology and Society,* **20(2), 12**. Published under license by the Resilience Alliance.

[5] Ors F. 2012. Environmental education and the role of media in environmental education in Turkey. *Procedia - Social and Behavioral Sciences*, **46**, 1339–1342.

[6] Uzuna F.V., Kelesa O. 2012. The effects of nature education project on the environmental awareness and behavior. *Procedia - Social and Behavioral Sciences,* **46**, 2912–2916.

[7] Giannoulis Chr., Skanavis C., Karapatsiou E. 2014. Environmental Awareness: Environmental Accidents as an Example to be Avoided. A Summative International Analysis. *Studies in Media and Communication.* Published by Redfame Publishing.

[8] Rodriguesa S.J. 2014. Environmental Education: A Propose of High School. *Procedia - Social and Behavioral Sciences*, **116**, 231–234.

[9] Frantz C., Mayer F.S. 2014. The importance of connection to nature in assessing environmental education programs. *Studies in Educational Evaluation,* **41**, 85–89.

[10] Hassana A., Osmanb K., Pudin S. 2009. The adults non-formal environmental education (EE): A Scenario in Sabah, Malaysia. *Procedia - Social and Behavioral Sciences,* **1**, 2306–2311.

[11] Saribas D., Teksoz G., Ertepinar H. 2014. The relationship between environmental literacy and self-efficacy beliefs toward environmental education. *Procedia - Social and Behavioral Sciences,* **116**, 3664–3668.

ISBN: 978-960-6865-94-7

[12] Skanavis C., Manolas E. 2015. School Gardens and Ecovillages: Innovative Civic Ecology Educational Approaches at Schools and Universities. Transformative Approaches to Sustainable Development at Universities, World Sustainability Series. *Springer International Publishing Switzerland.* DOI 10.1007/978-3-319-08837-2_37.

[13] Tayci F., Uysal F. 2012. A study for determining the elementary school students' environmental knowledge and environmental attitude level. *Procedia - Social and Behavioral Sciences*, **46**, 5718–5722.

[14] Srbinovski M., Erdogan M., Ismailia M. 2010. Environmental literacy in the science education curriculum in Macedonia and Turkey. *Procedia - Social and Behavioral Sciences*, **2**, 4528–4532.

[15] http://www.ekke.gr/estia/gr_pages/F_synerg/Mpotsaris_N_PE/Nom_PE_Mpotsaris_06.pdf (accessed July 31st , 2015)

[16] http://www.kalyterizoi.gr/ (accessed April 21st, 2016)

[17] http://www.futurelibrary.gr/ (accessed April 21st, 2016)

[18] Singh H., Rahman S. 2012. An Approach for Environmental Education by Non-Governmental Organizations (NGOs) in Biodiversity Conservation. *Procedia - Social and Behavioral Sciences,* **42**, 144–152.

[19] Zsóka Á., Szerényi Z.M., Széchy A., Kocsis T. 2013. Greening due to environmental education? Environmental knowledge, attitudes, consumer behavior and everyday pro-environmental activities of Hungarian high school and university students. *Journal of Cleaner Production*, **48**, 126–138.

[20] Bamberg S., Moser G. 2007. Twenty years after Hines, Hungerford, and Tomera: A new meta-analysis of psycho-social determinants of pro-environmental behavior. *Journal of Environmental Psychology,* **27**, 14–25.

[21] Osbaldiston R., Sheldon K.M. 2003. Promoting internalized motivation for environmentally responsible behavior: A prospective study of environmental goals. *Journal of Environmental Psychology*, **23**, 349–357.

[22] Carleton-Hug A., Hug J.W. 2010. Challenges and opportunities for evaluating environmental education programs. *Evaluation and Program Planning,* **33Q**, 159-164.

[23] Simmons B. et al. 2009. Nonformal environmental education programs: Guidelines for Excellence. *North American Association for Environmental Education,* USA.

[24] Byron M., et al. 2014. Measuring environmental education outcomes. Russ A. (Ed.). (2014). Washington, DC: North American Association for Environmental Education.

[25] Kobori H., Dickinson J.L., Washitani I., Sakurai R., Amano T., Komatsu N., Kitamura W., Takagawa Sh., Koyama K., Ogawara T., Miller-Rushing A. J., 2015. Citizen science: a new approach to advance ecology, education, and conservation. *This article is published with open access at Springerlink.com.* DOI 10.1007/s11284-015-1314-y.

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